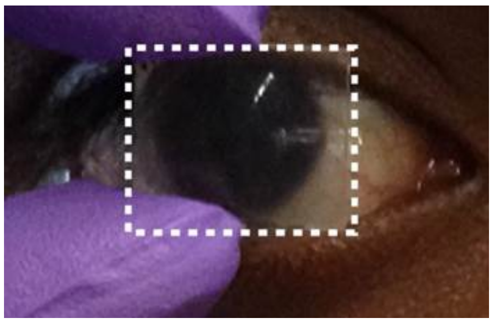
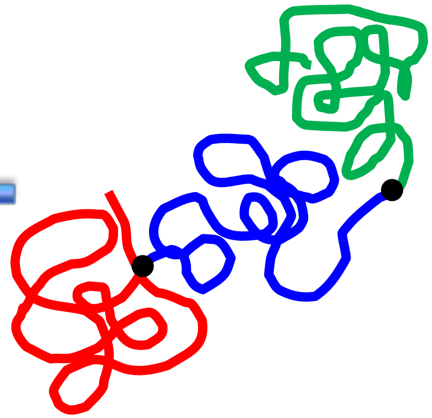
Designing Functional Polymers for Water Purification and Flexible Electronic Applications

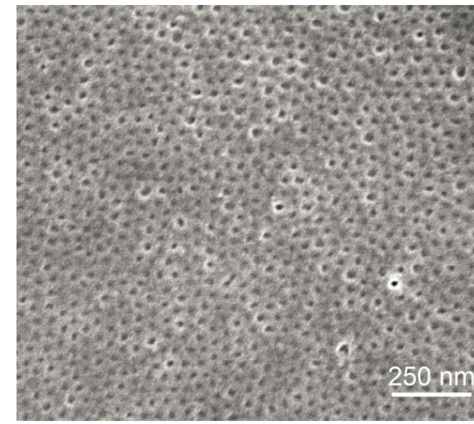
<u>Transparent Conducting Glasses</u>



<u>Functional Homopolymers and Block Polymers</u>



<u>Nanoporous Block Polymer-based Membranes</u>



Bryan W. Boudouris

Davidson School of Chemical Engineering and Department of Chemistry
Purdue University

SURF Program Seminar
Tuesday, June 26, 2018

Contact: boudouris@purdue.edu; @Boudouris_Group

Organic Electronic Devices Require Transparent Conductors

Organic Light-emitting Device (OLED) Displays

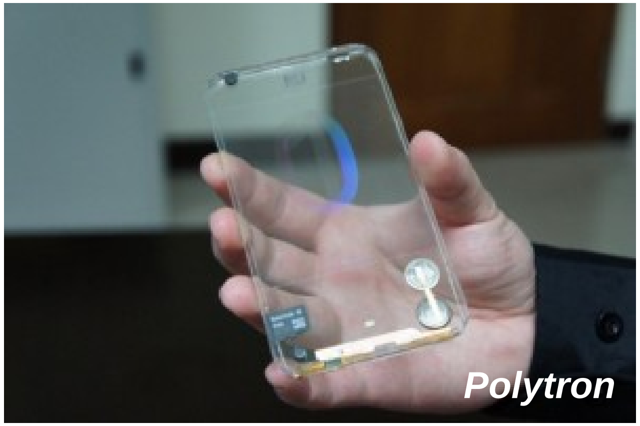
Thin and Lightweight

LG

Flexible

Samsung

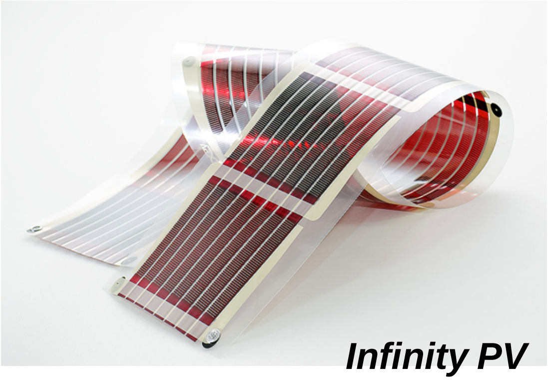
Transparent



Polytron

Organic Photovoltaic (OPV) Devices

Large Area Production



Infinity PV

Portable Applications

Konarka

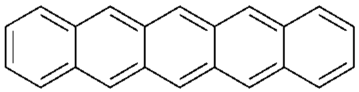
Conformal Coverage

Heliatek

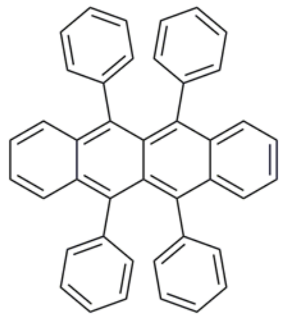
Organic Electronic Materials Generally Are Highly Conjugated

Small Molecule Semiconductors

p-type Materials



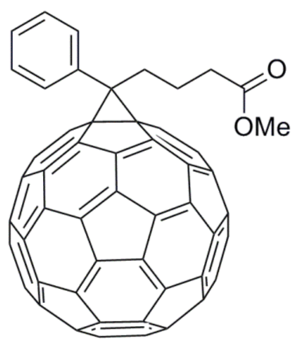
Pentacene



Rubrene

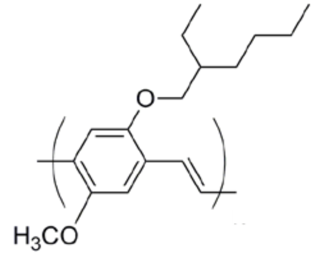
n-type Materials

Buckminsterfullerene

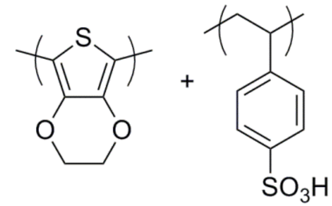


PCBM

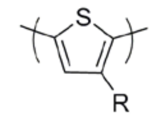
Polymeric Semiconductors/Conductors



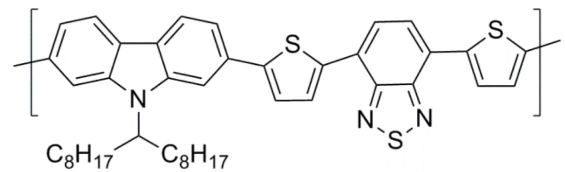
MEH-PPV



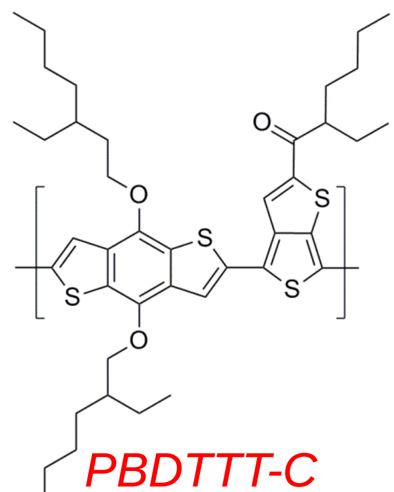
PEDOT:PSS



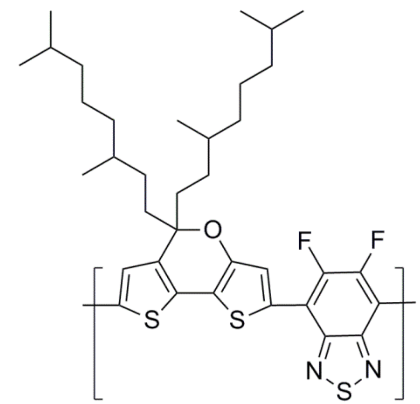
P3AT



PCDTBT



PBDTTT-C

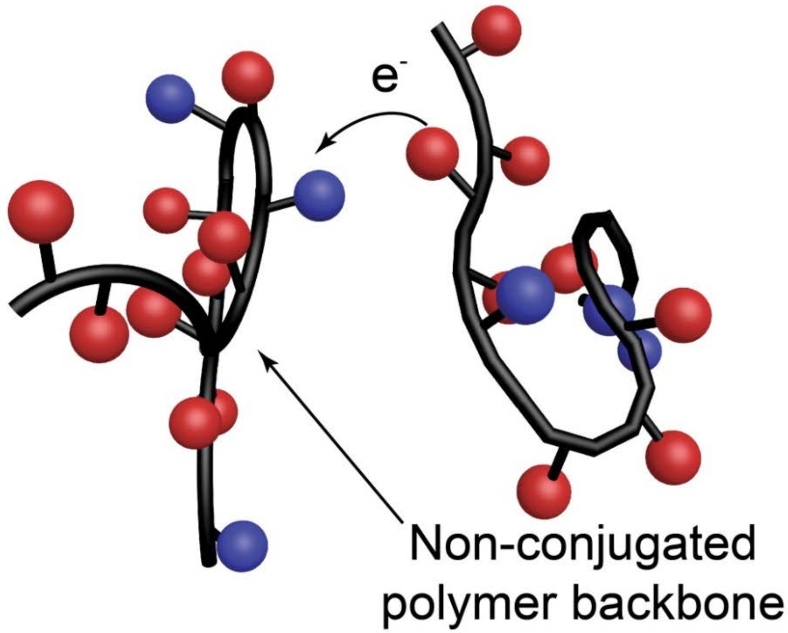


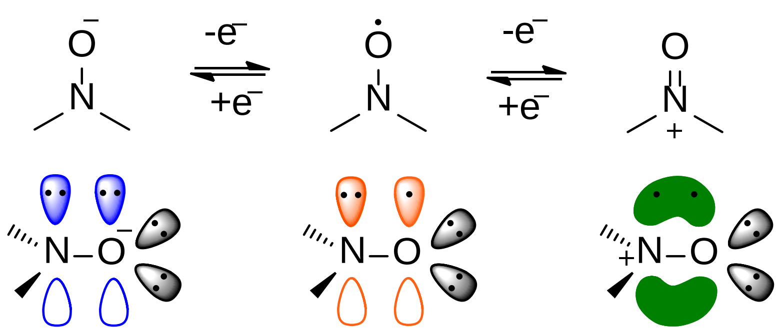
PDTP-DFBT

Boudouris, B. W. *Curr. Opin. Chem. Eng.* **2013**, *2*, 294.

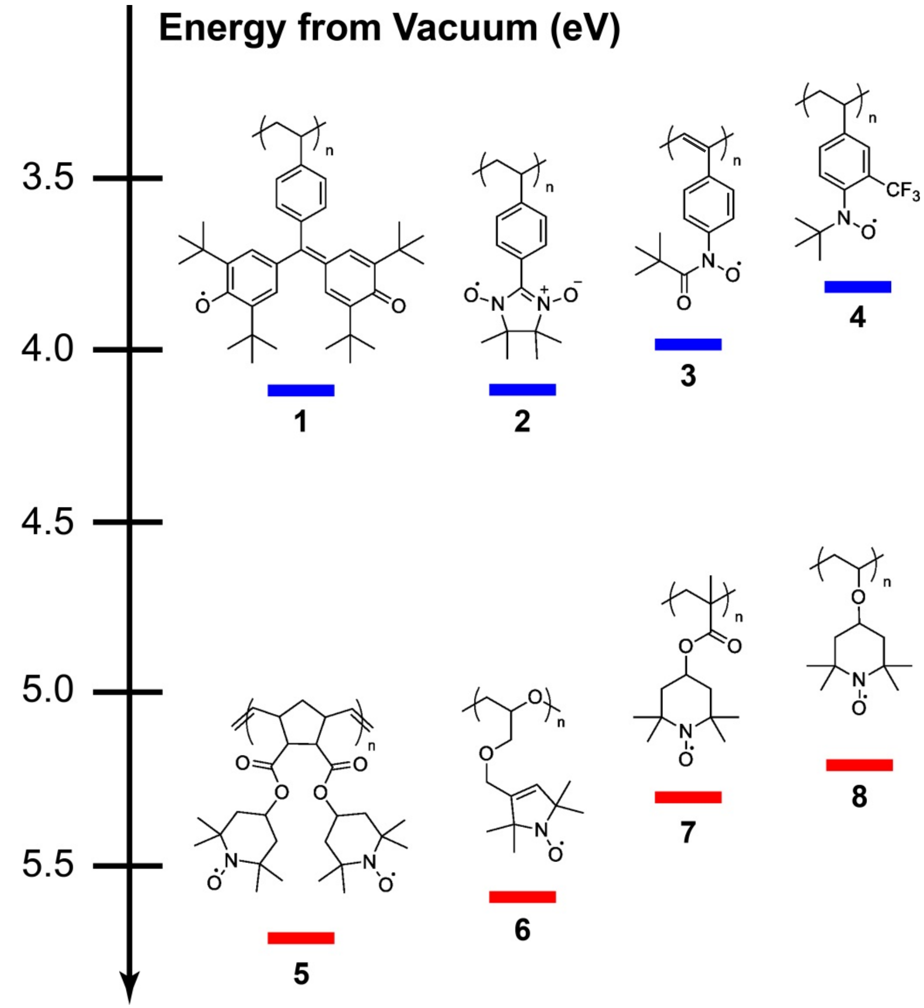
Radical Polymers Break the Conjugated Polymer Paradigm

Radical Polymers Conduct through Local Oxidation-Reduction Sites



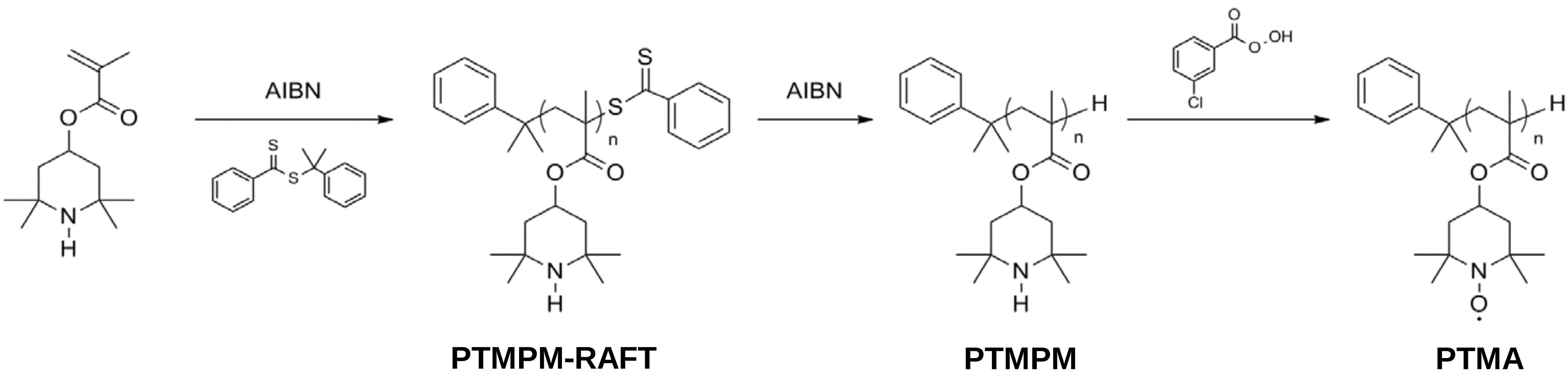


Tunable Charge Transport Levels

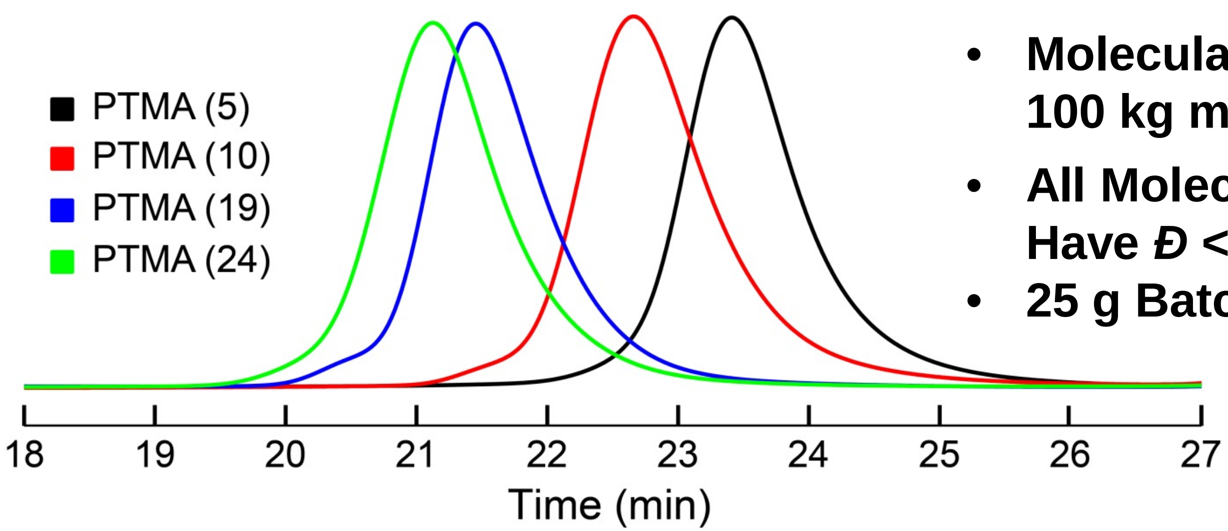


Tomlinson, E. P.; Hay, M. E.; Boudouris, B. W. *Macromolecules* **2014**, *47*, 6145.
Wingate, A. J.; Boudouris, B. W. *J. Polym. Sci. Part A* **2016**, *54*, 1875.

Radical Polymers Synthesized Using a Controlled Route



<u>PTMA Synthesis is Much More Flexible Than That of Most Conjugated Polymers</u>

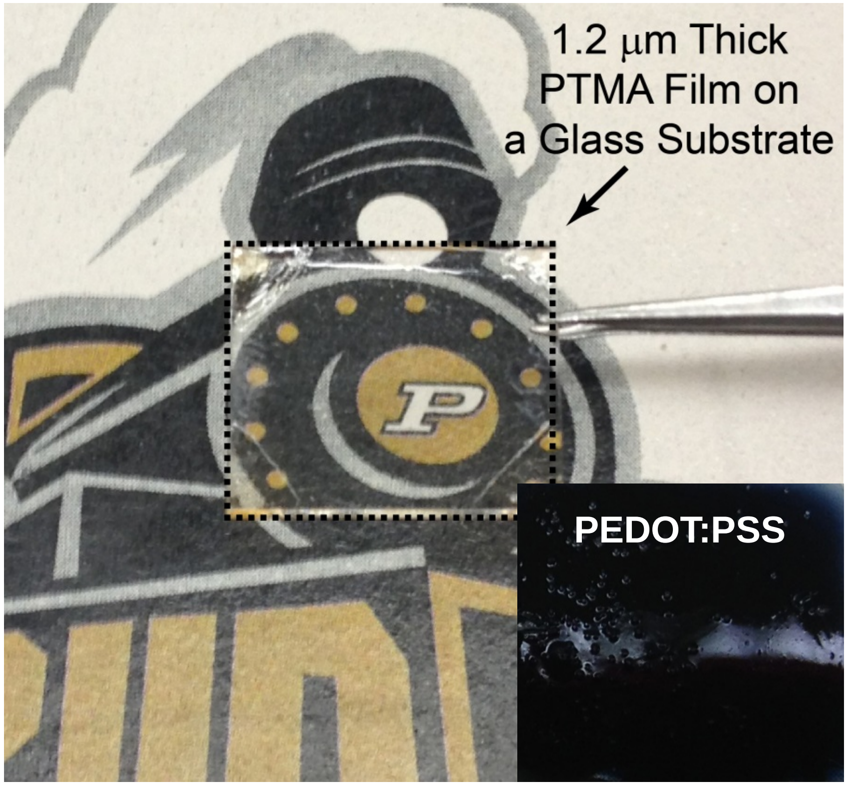


- **Molecular Weights Between 5 and 100 kg mol^{-1} Synthesized Readily**
- **All Molecular Weight Distributions Have *Đ* < 1.2**
- **25 g Batches Synthesized in 3 days**

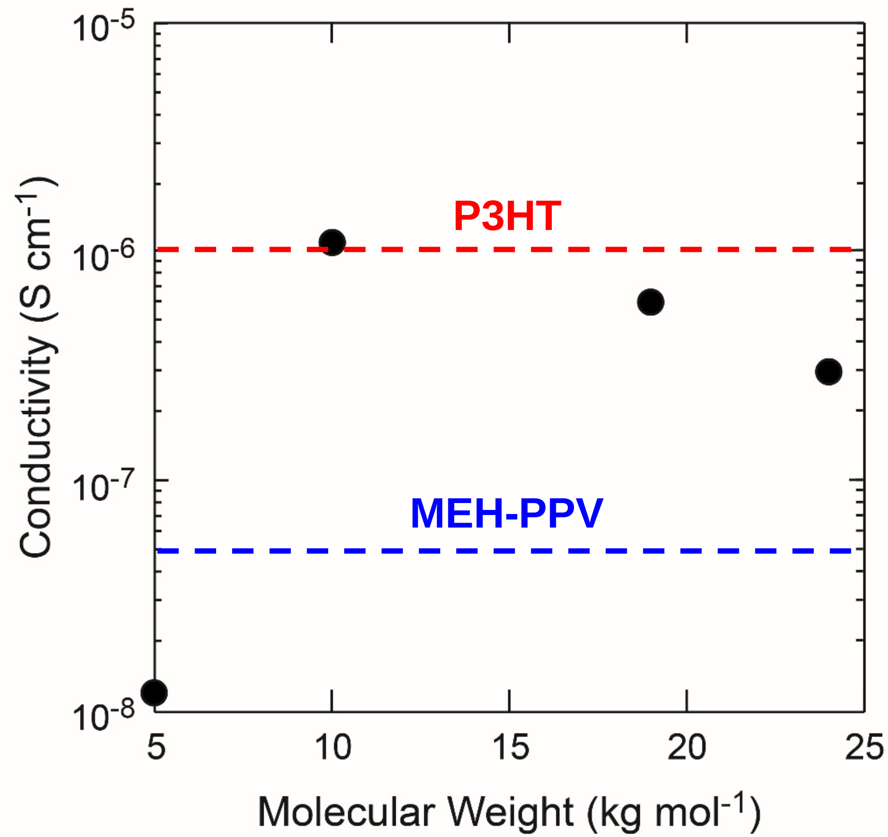
Rostro, L.; Baradwaj, A. G.; Boudouris, B. W. *ACS Appl. Mater. Interfaces* **2013**, *5*, 9896.

PTMA Presents as a Transparent, Charge Carrying Polymer

PTMA Films Are Transparent



PTMA Films Conduct



Films were generated by spin-coating 100 mg of solid from 1 mL of chloroform at a rotation rate of 600 rpm
This led to films of ~1.2 μm, as measured using a profilometer

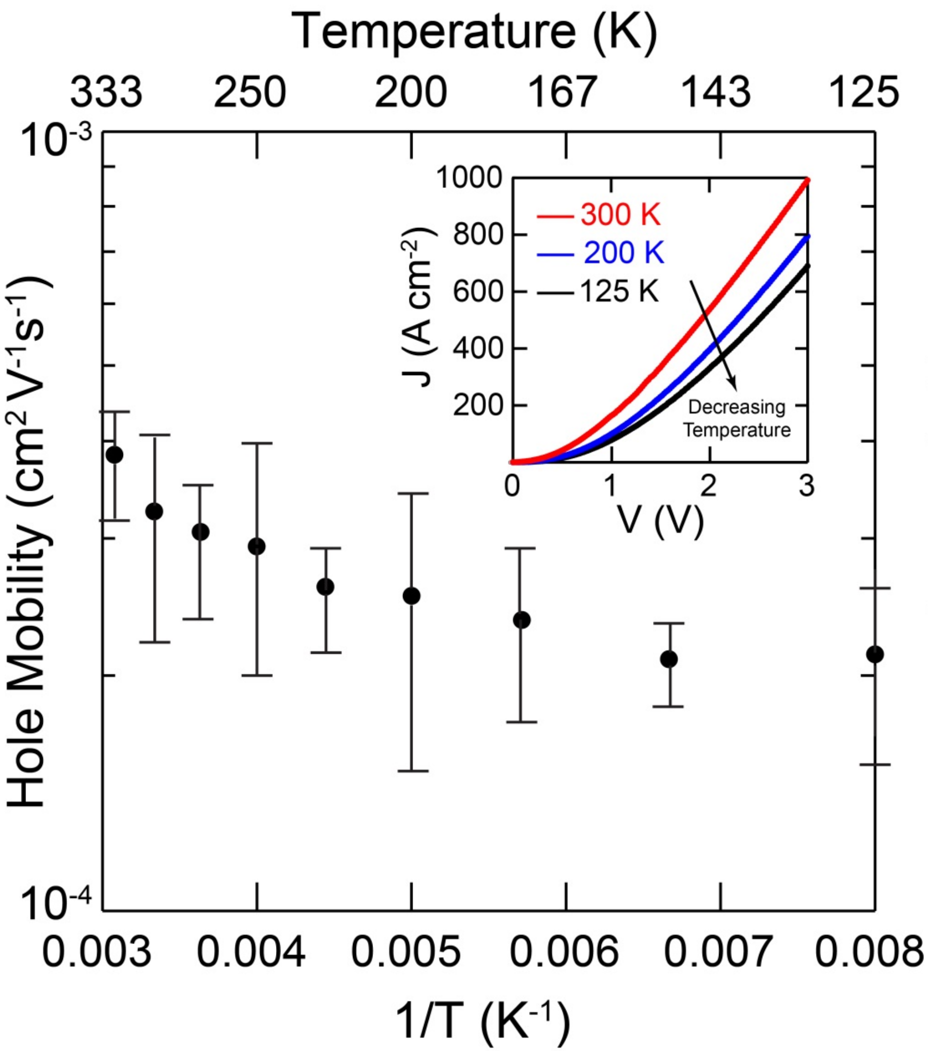
Ltaief, A.; Bouazizi, A.; Davenas, J.; Chaabane, R. B.; Ouada, B. H. *Syn. Met.* **2004**, *147*, 261.

Gearba, I. R.; Nam, C.Y.; Pindak, R.; Black, C. T. *Appl. Phys. Lett.* **2009**, *95*, 173307.

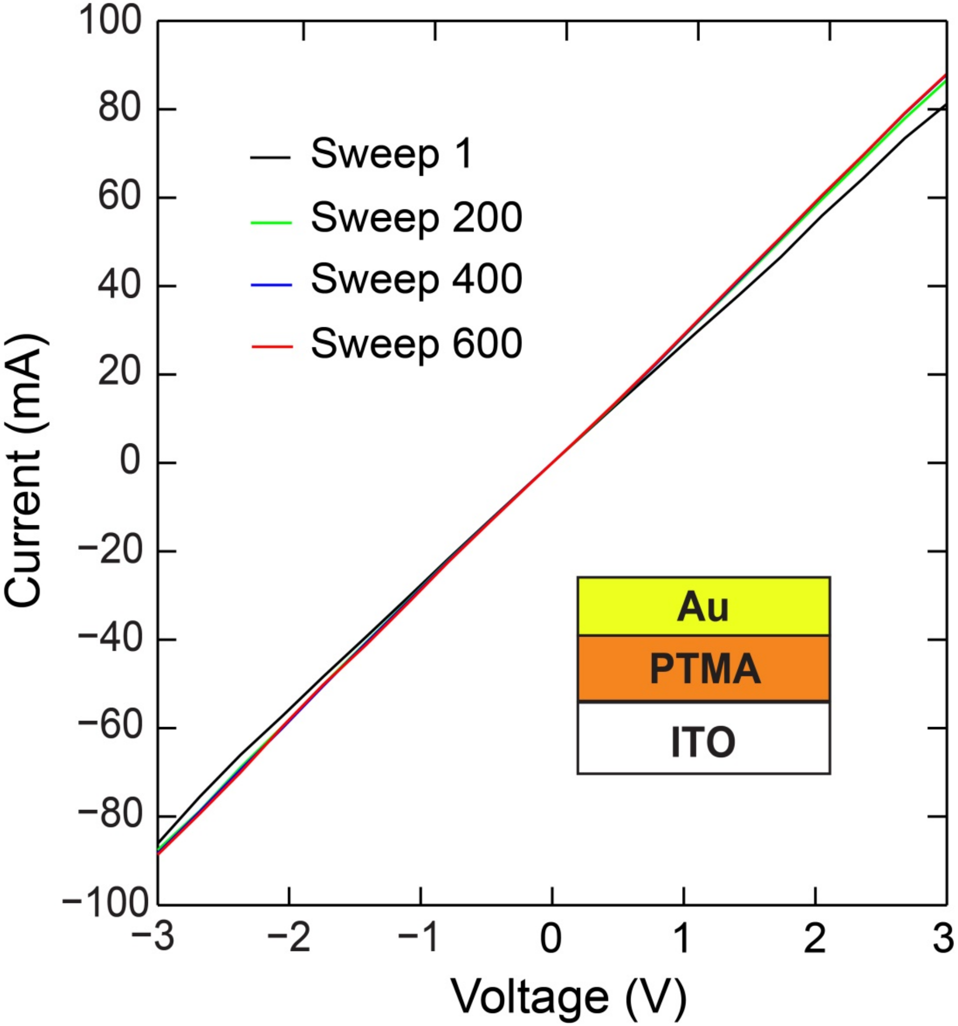
Rostro, L.; Baradwaj, A. G.; Boudouris, B. W. *ACS Appl. Mater. Interfaces* **2013**, *5*, 9896.

PTMA Has a Temperature-Independent Mobility and is Durable

Temperature-Independent Transport



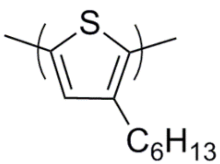
Long-Lasting Performance



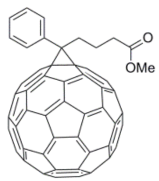
Baradwaj, A. G.; Rostro, L.; Alam, M. A.; Boudouris, B. W. *Appl. Phys. Lett.* **2014**, *104*, 213306.

Baradwaj, A. G.; Rostro, L.; Boudouris, B. W. *Macromol. Chem. Phys.* **2016**, *217*, 477.

Device Stability with P3HT:PCBM Inverted Solar Cells

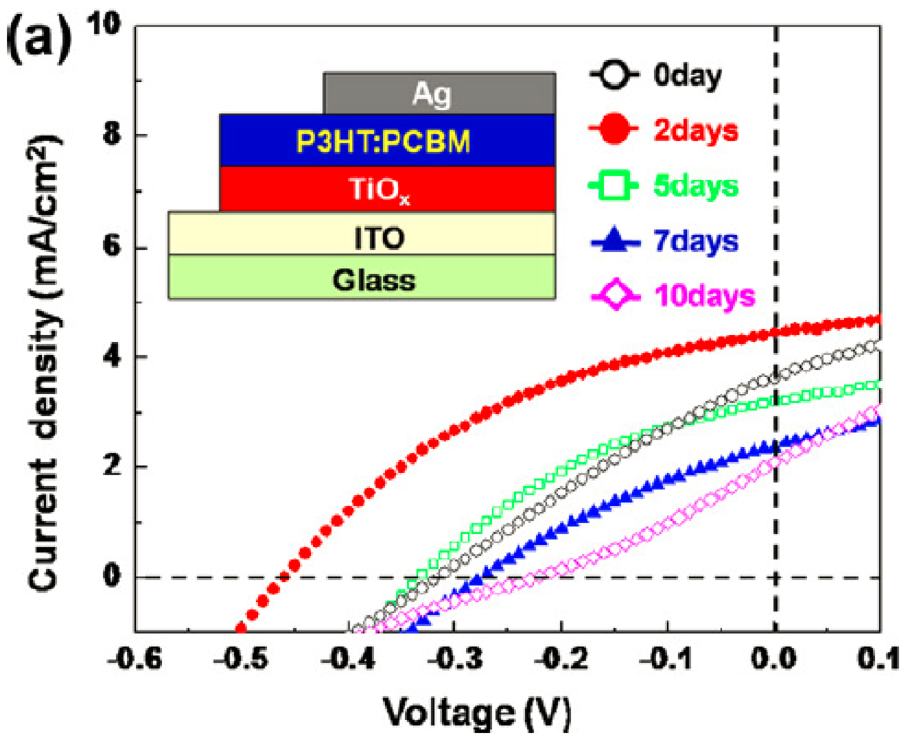


P3HT (p-Type)

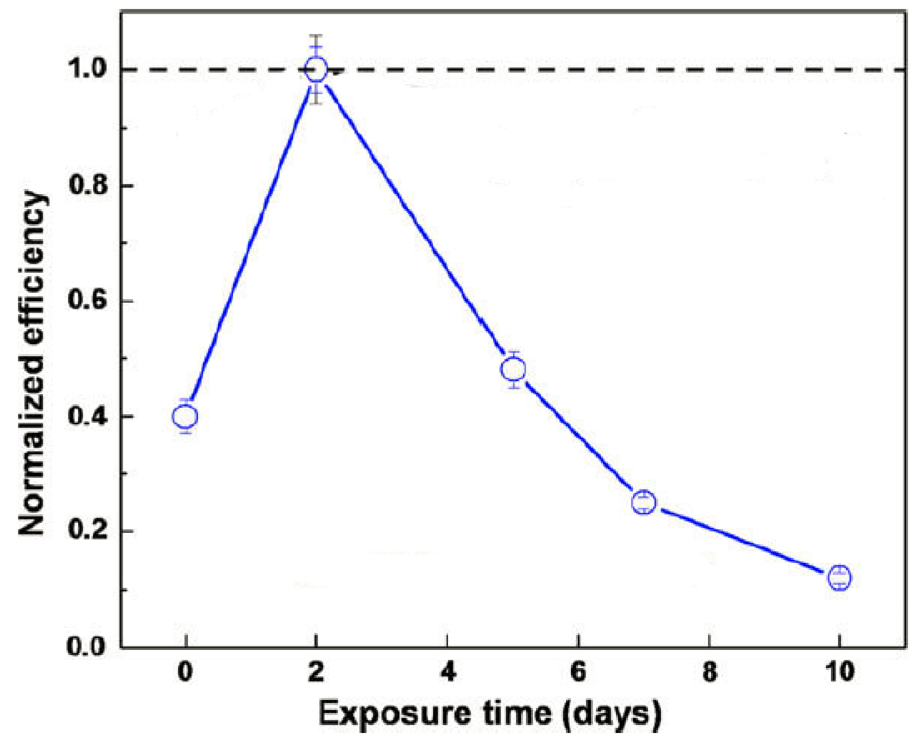


PCBM (n-Type)

Performance of OPVs Change with Ambient Exposure



Performance Peaks After 2 Days of Exposure to Ambient

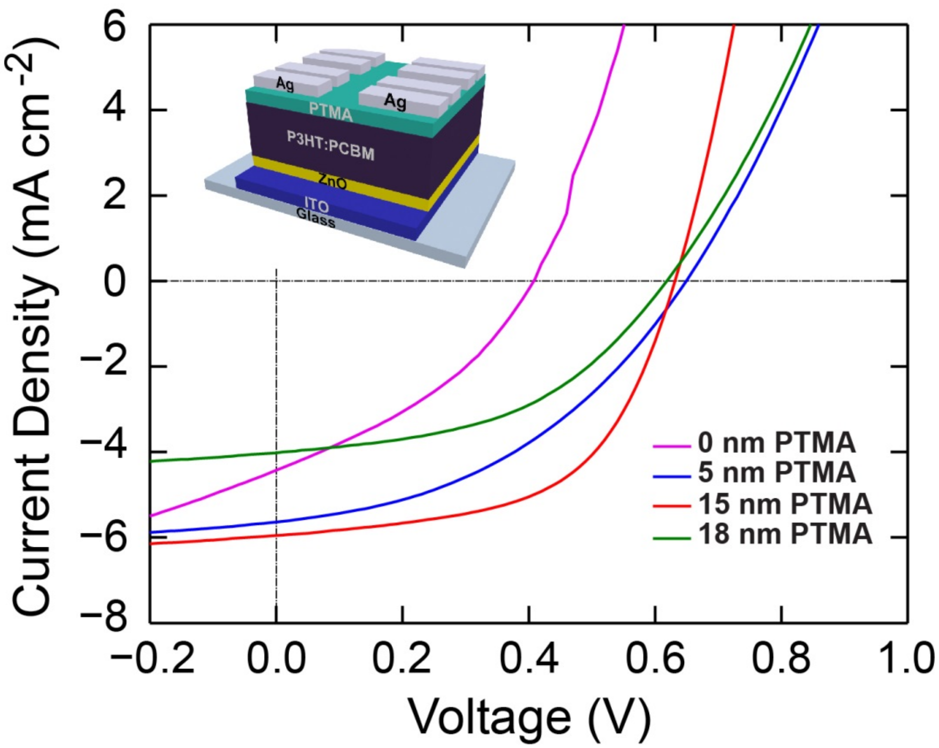


Can We Stabilize the Behavior of the OPV Devices through the Interlayers?

Kim, C. S.; Kim, J. B.; Lee, S. S.; Kim, Y. S.; Loo, Y.-L. *Org. Electron.* **2009**, *10*,1483.

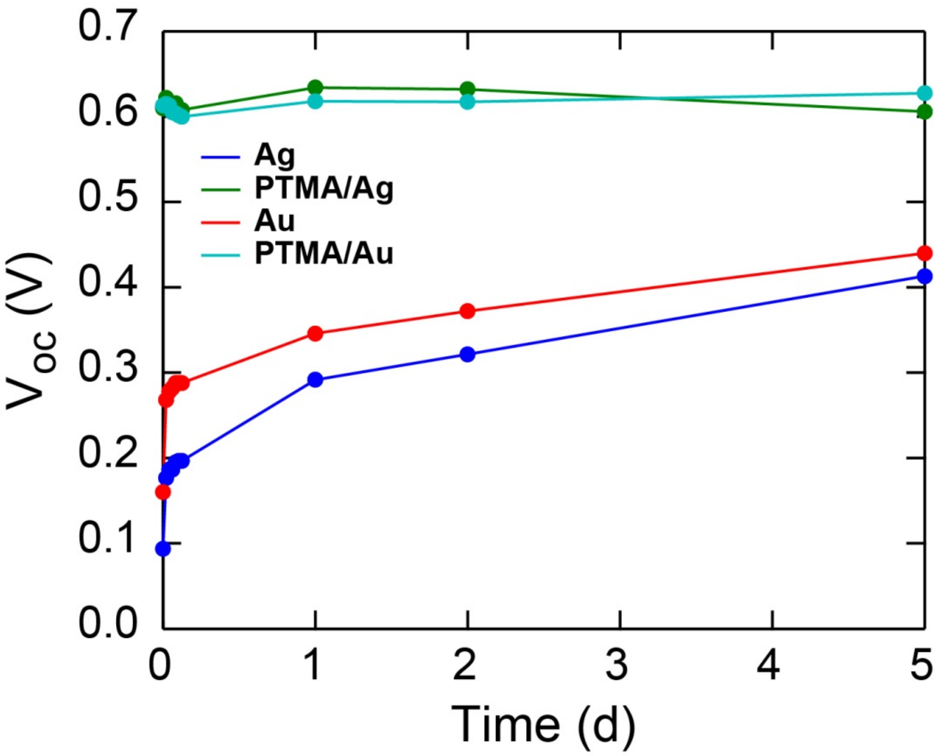
PTMA Improves the Performance and Stability of OPVs

PTMA Improves the Device Performance of Inverted OPV Devices with 5 Days of Exposure to Ambient Conditions



15 nm is the Optimal PTMA Thickness for this Types of Inverted OPV Devices

Optimized PTMA Coating Leads to a Time-Independent Open-Circuit Voltage (V_{oc})

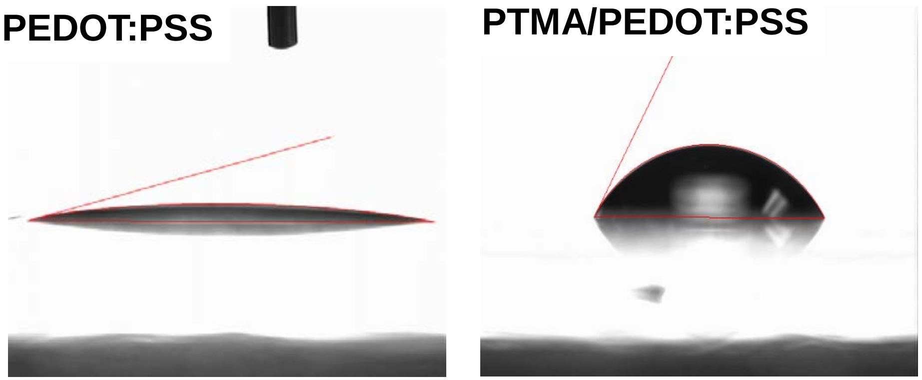


Addition of PTMA Pins the HOMO Level of the P3HT to Fix the V_{oc} Independent of the Metal Used

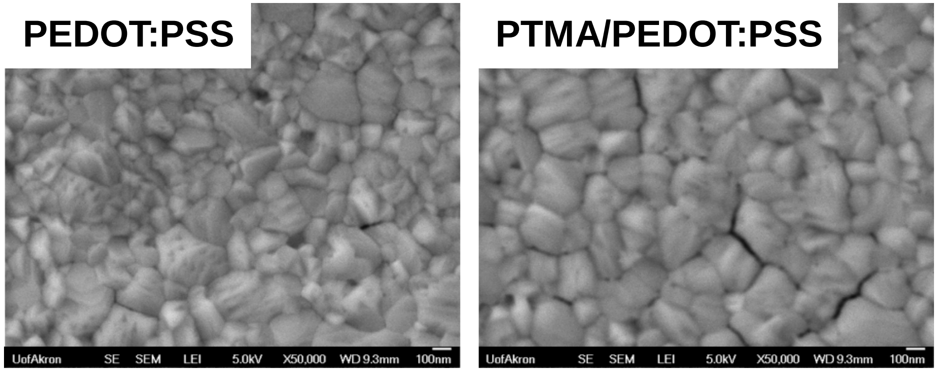
Rostro, L.; Galicia, L.; Boudouris, B. W. *J. Polym. Sci. Part B: Polym. Phys.* **2015**, *53*, 311.

PTMA Also Modifies Interfaces in Perovskite Solar Cells

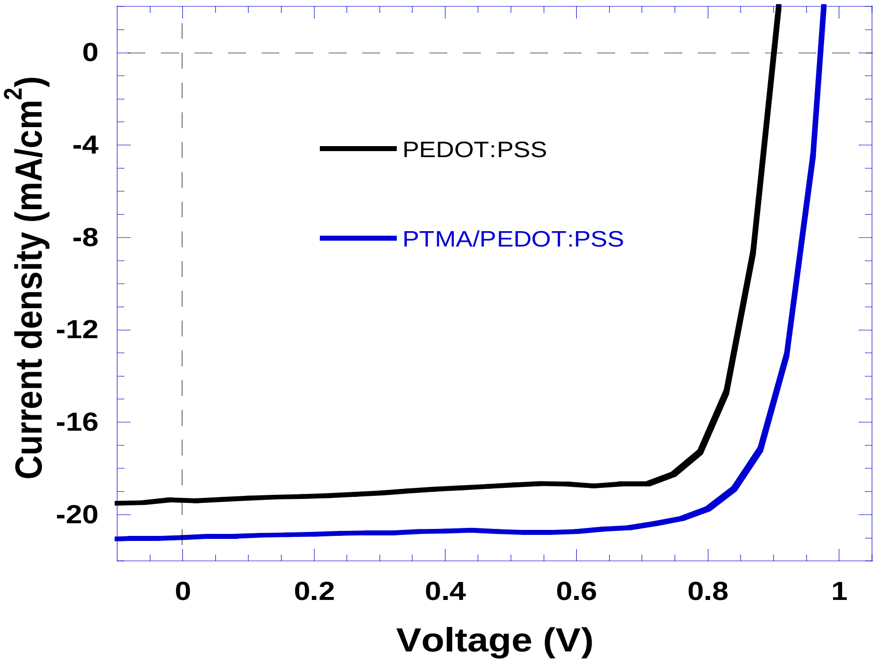
PTMA Modifies the Perovskite Growth Substrate Surface Energy



Perovskite Materials Grown on PTMA Have Larger Grains Than When They are Grown on PEDOT:PSS



Inclusion of PTMA Interlayer Improves Device Performance and Stability

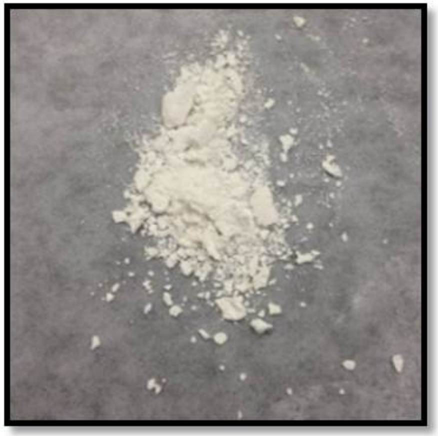


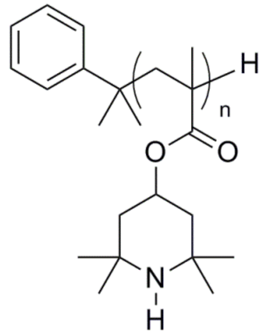
HTL	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE(%)
PEDOT:PSS	0.91	19.38	0.77	13.64
PTMA/PEDOT:PSS	0.96	20.99	0.79	15.86

Device Stability Increased by ~4-fold with the Inclusion of the PTMA Interlayer

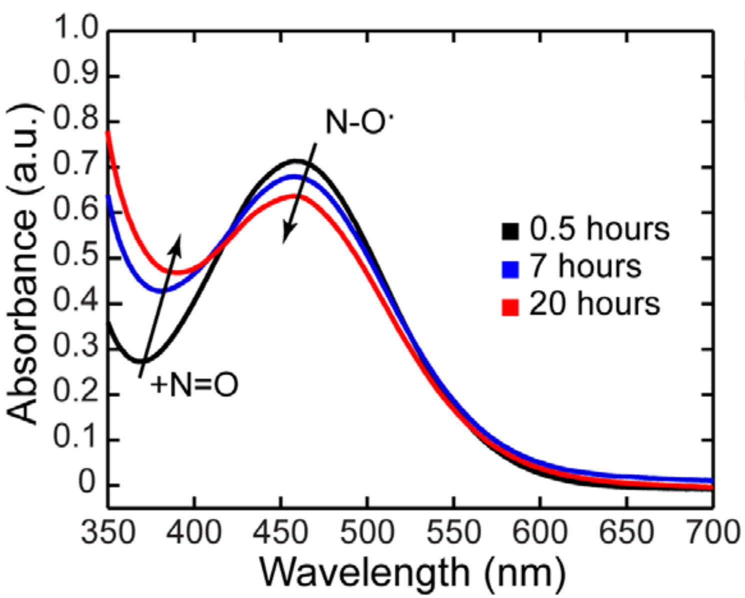
Zheng, L.; Mukherjee, S.; Wang, K.; Hay, M. E.; Boudouris, B. W.; Gong, X. *J. Mater. Chem. A* **2017**, *5*, 23831.

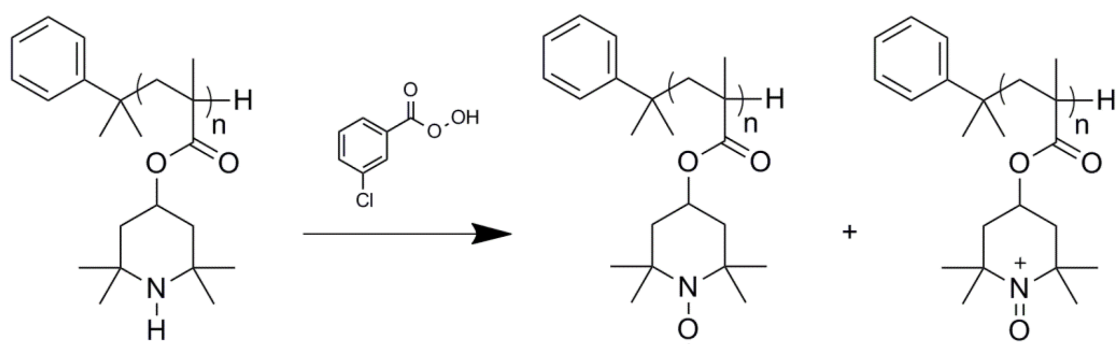
Radical Polymers Synthesized Using a Controlled Route





The Deprotection of PTMPM and the Oxidation of PTMA is a Crucial Step





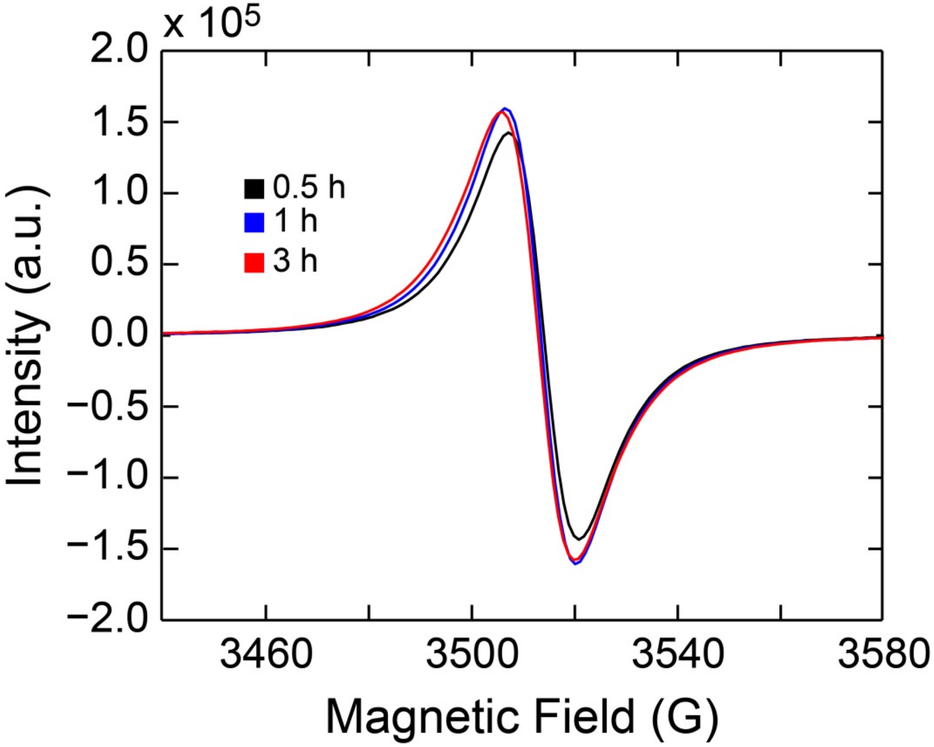
PTMPM **PTMA** **PTMA+**

Spectra Acquired with 30 mg PTMA in 1 mL chloroform

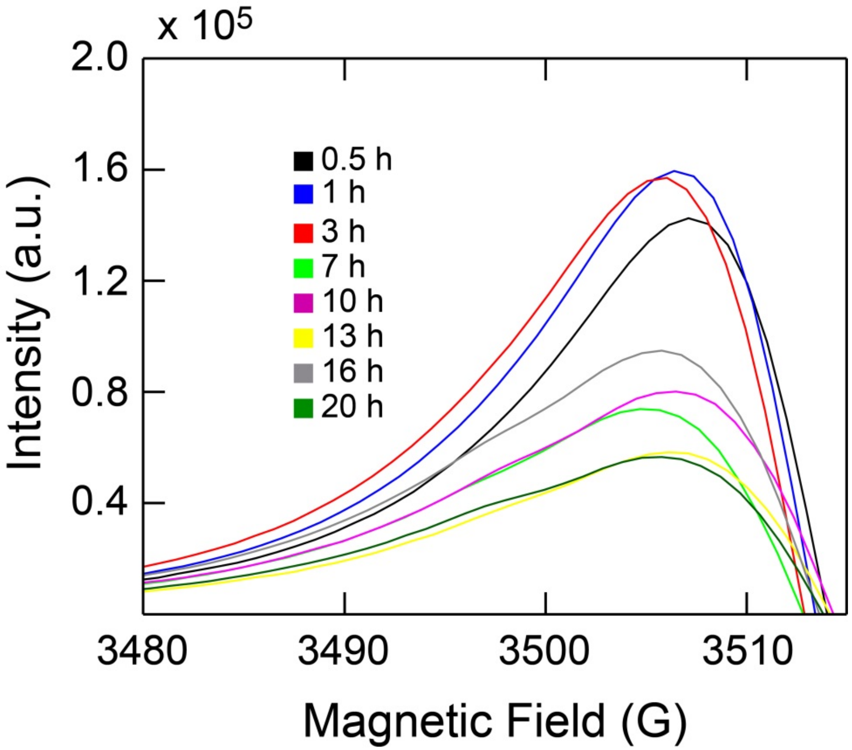
Rostro, L.; Baradwaj, A. G.; Boudouris, B. W. *ACS Appl. Mater. Interfaces* **2013**, *5*, 9896.

EPR Spectroscopy Shows a Change in Radical Density

Radical Concentration Changes as a Function of Oxidation Time



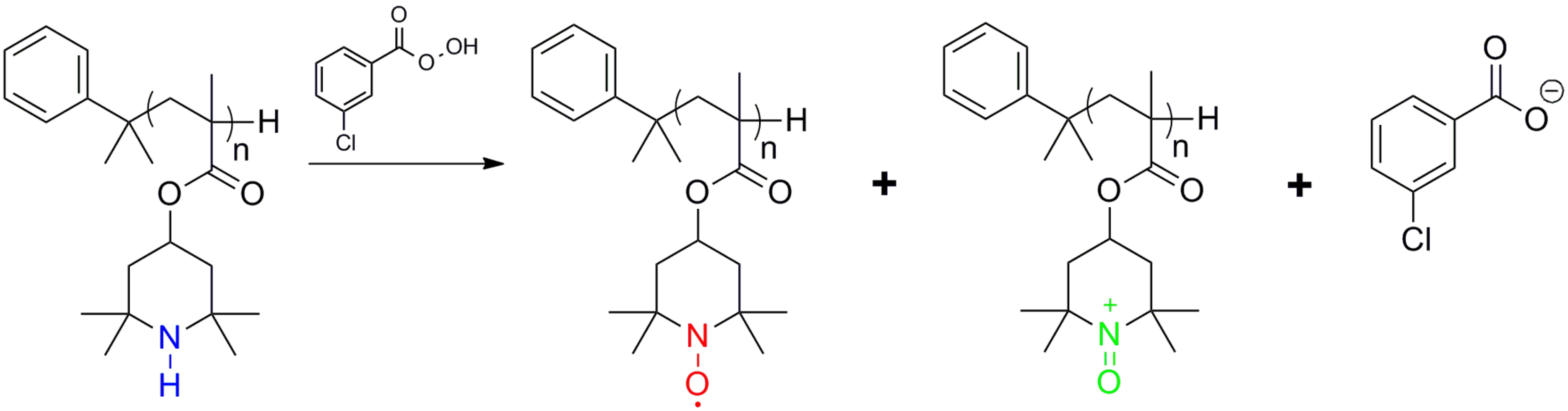
There is a Clear Maximum in the Radical Density at Shorter Oxidation Times



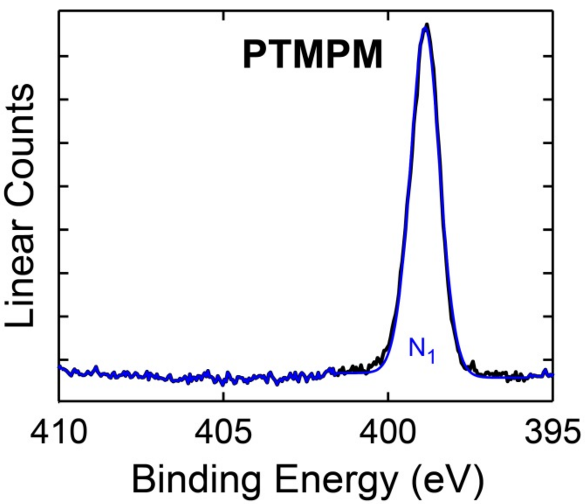
What Happens to the Radical Groups?

Rostro, L.; Wong, S. H.; Boudouris, B. W. *Macromolecules* **2014**, *47*, 3713.

X-Ray Photoelectron Spectroscopy Confirms PTMA+



N_1 **N_2** **N_3**

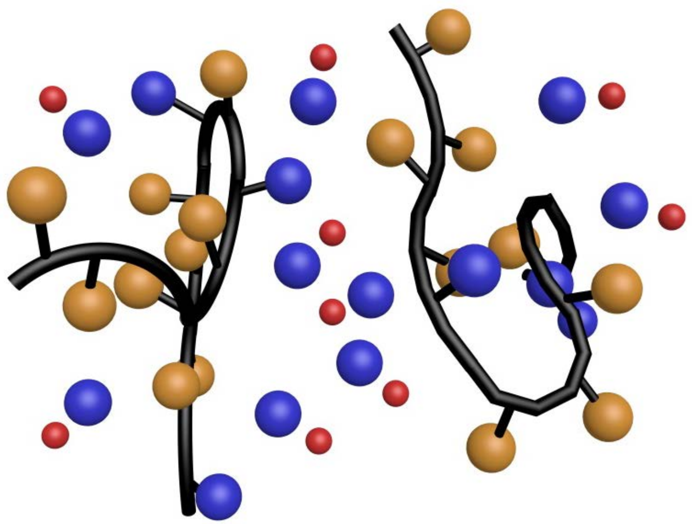


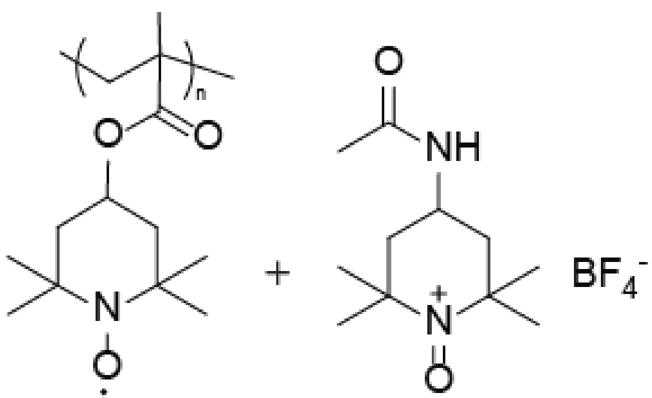
This Unintentional Dopant was Improving Charge Transport

Rostro, L.; Wong, S. H.; Boudouris, B. W. *Macromolecules* **2014**, *47*, 3713.

Addition of an Oxoammonium Cation Small Molecule

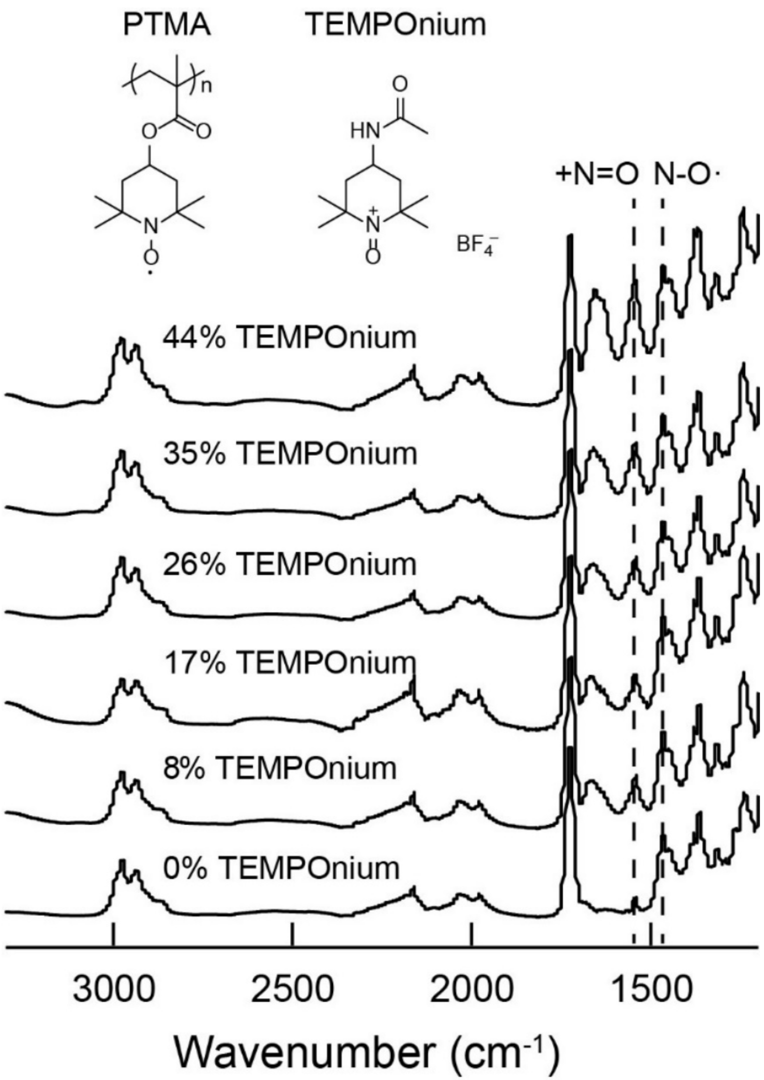
Small Molecule Doping of PTMA with TEMPOnium





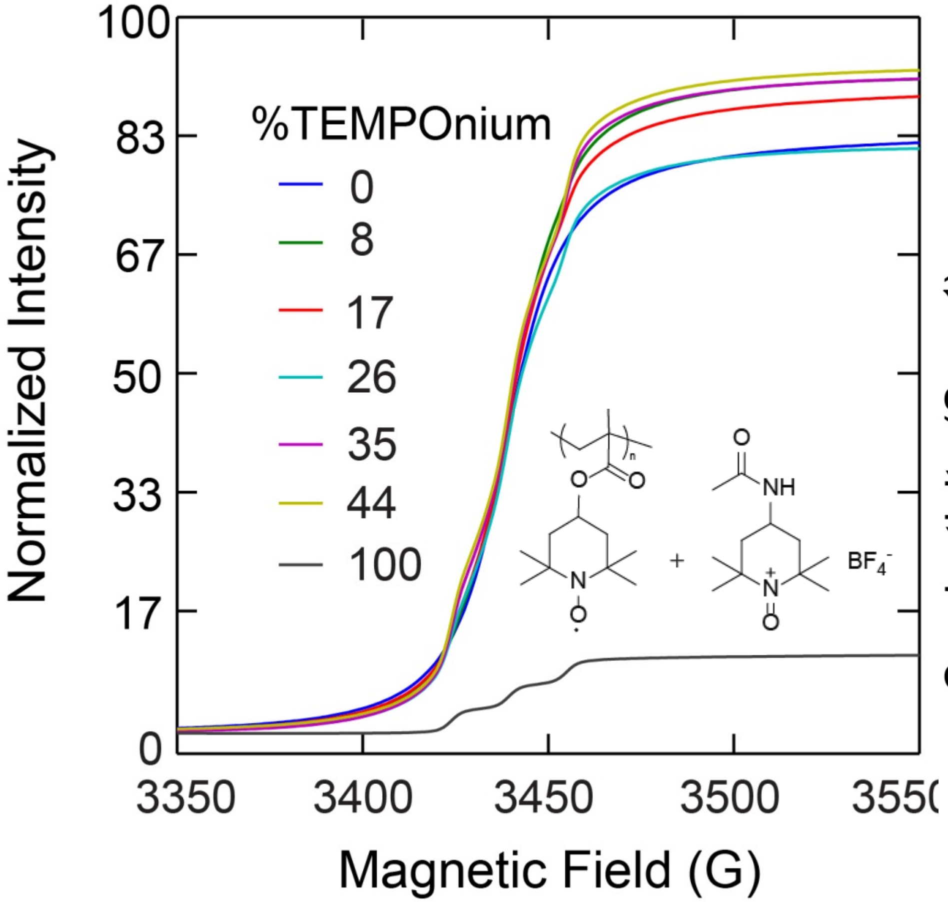
4-acetamido-2,2,6,6-tetramethyl-1-oxopiperidinium tetrafluoroborate (TEMPOnium)

Radical and Cation Functionalities are Present in the Thin Films

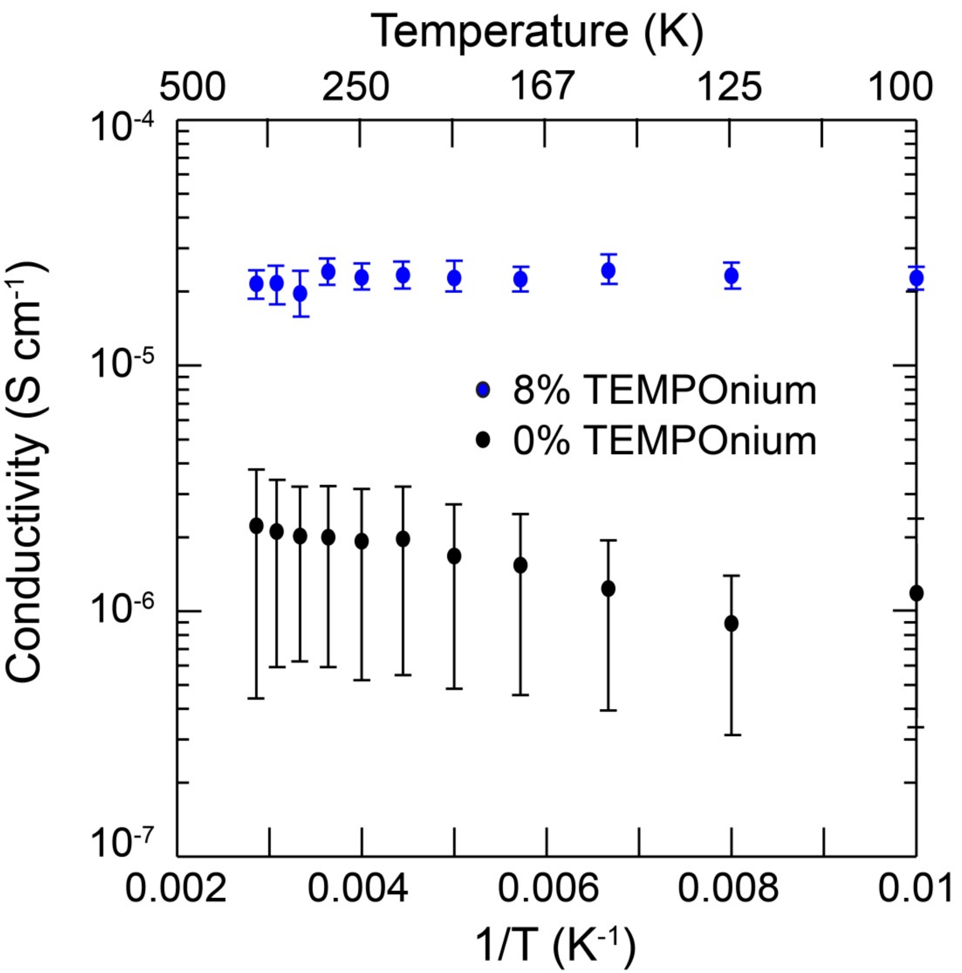


Redox-Active Salts Increase the Electrical Conductivity of PTMA

Radical Density is not Inhibited by Addition of TEMPOnium



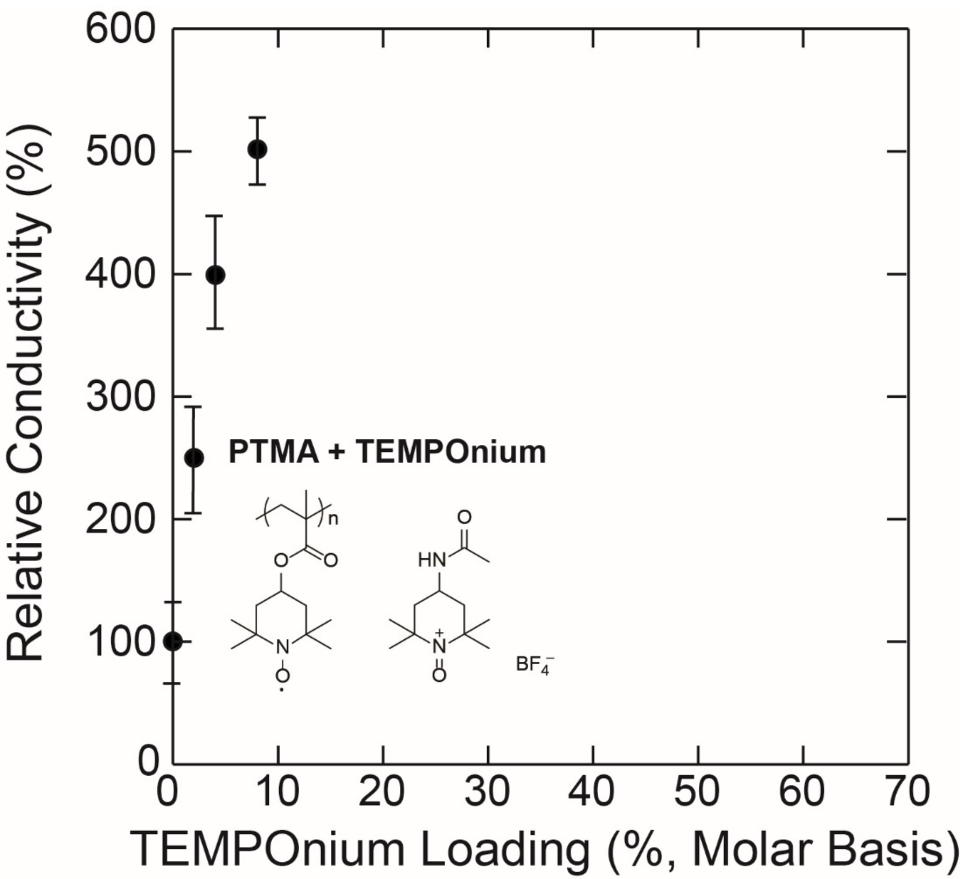
There is No Temperature Dependence for Transport



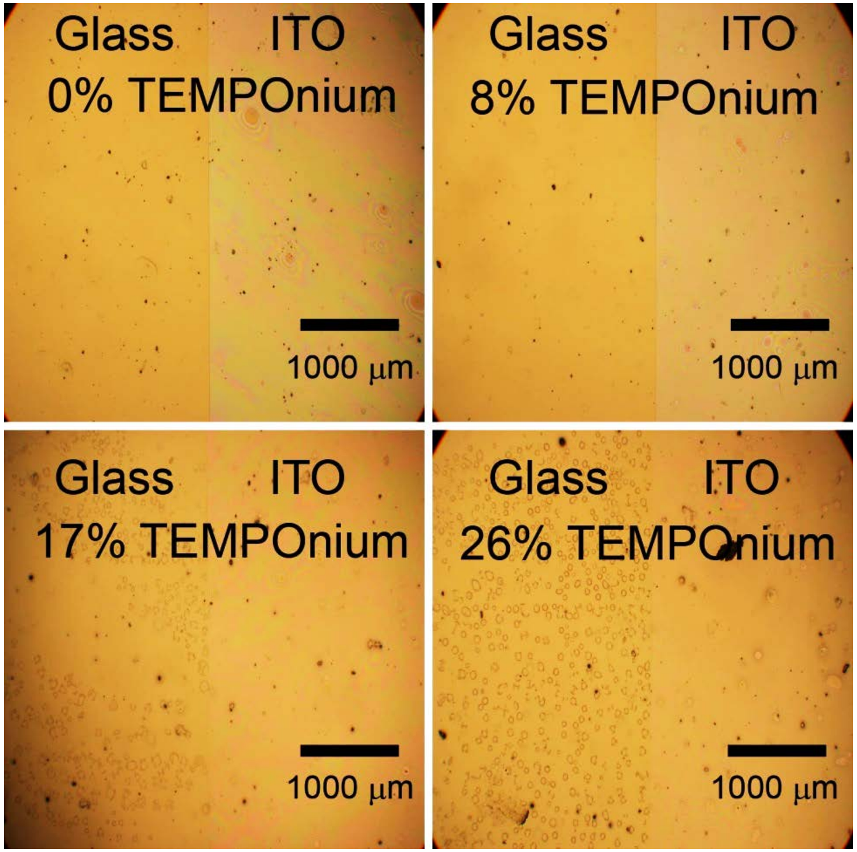
Baradwaj, A. G.; Wong, S. H.; Laster, J. S.; Wingate, A. J.; Hay, M. E.; Boudouris, B. W. *Macromolecules* **2016**, *49*, 4784.

Small Molecule Doping Allows for Conductivity Tuning

Addition of TEMPOnium Results in 5x Increase in Conductivity



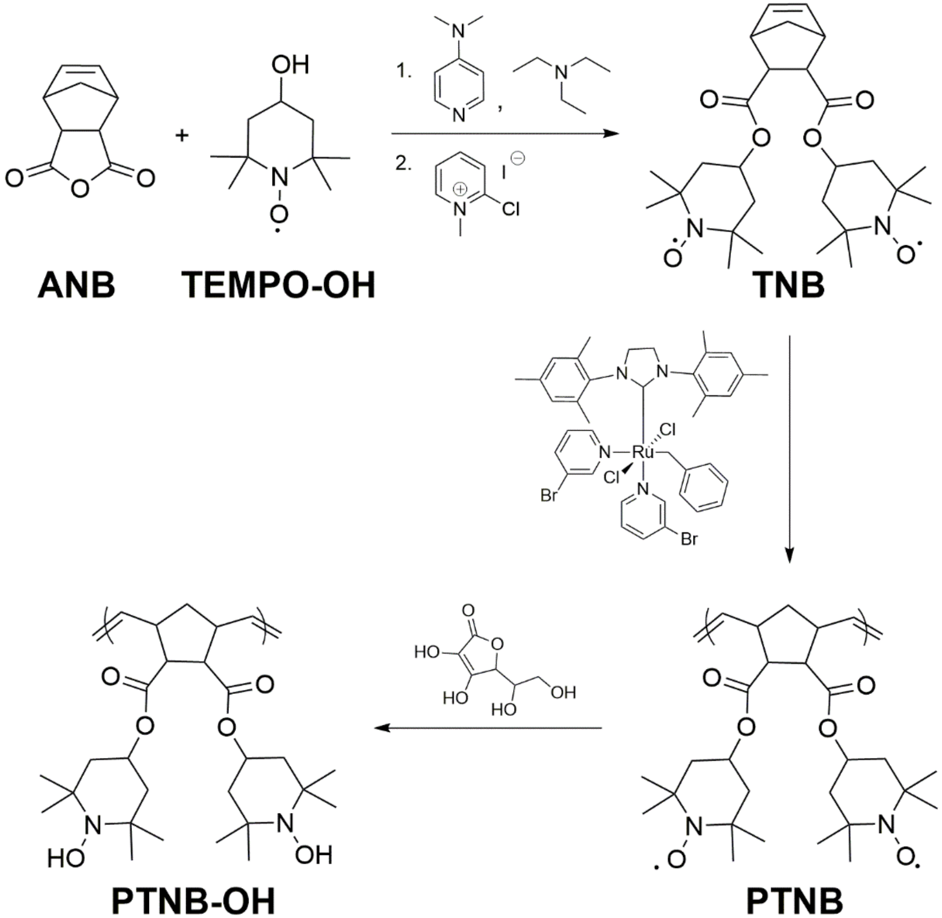
Increasing Levels of TEMPOnium Leads to Poor Film Quality



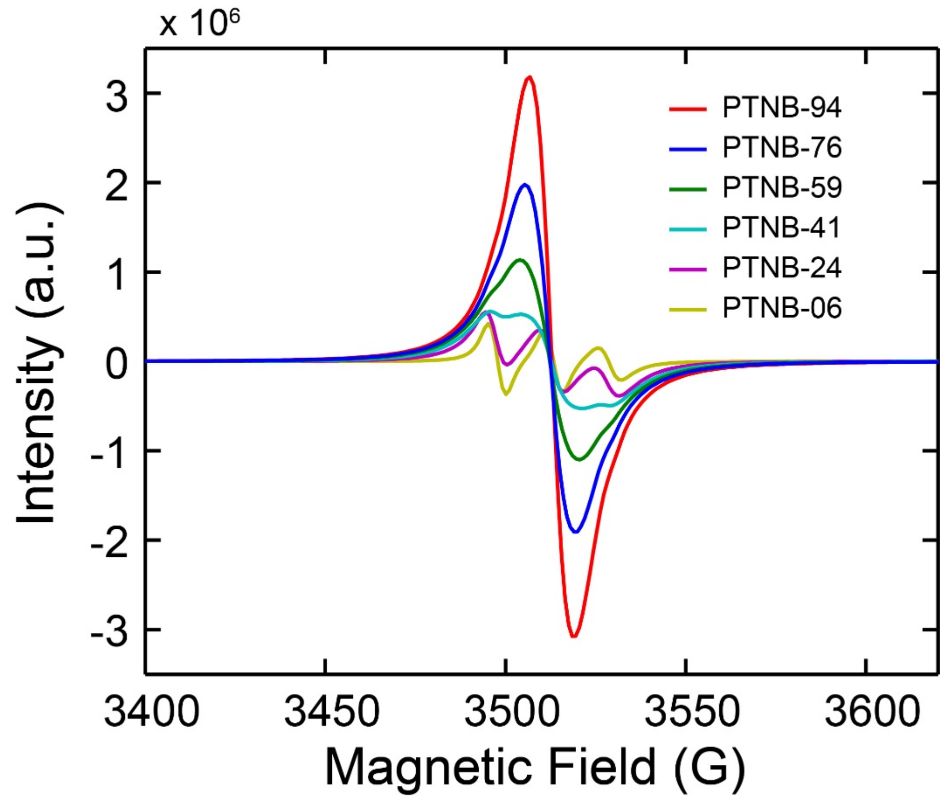
Baradwaj, A. G.; Wong, S. H.; Laster, J. S.; Wingate, A. J.; Hay, M. E.; Boudouris, B. W. *Macromolecules* **2016**, *49*, 4784.

ROMP-Mediated Schemes Allow for Control of Radical Groups

PTNB is a Functional Polymer and PTNB-OH is Electronically-Insulating



Blending PTNB and PTNB-OH Controls Radical Density

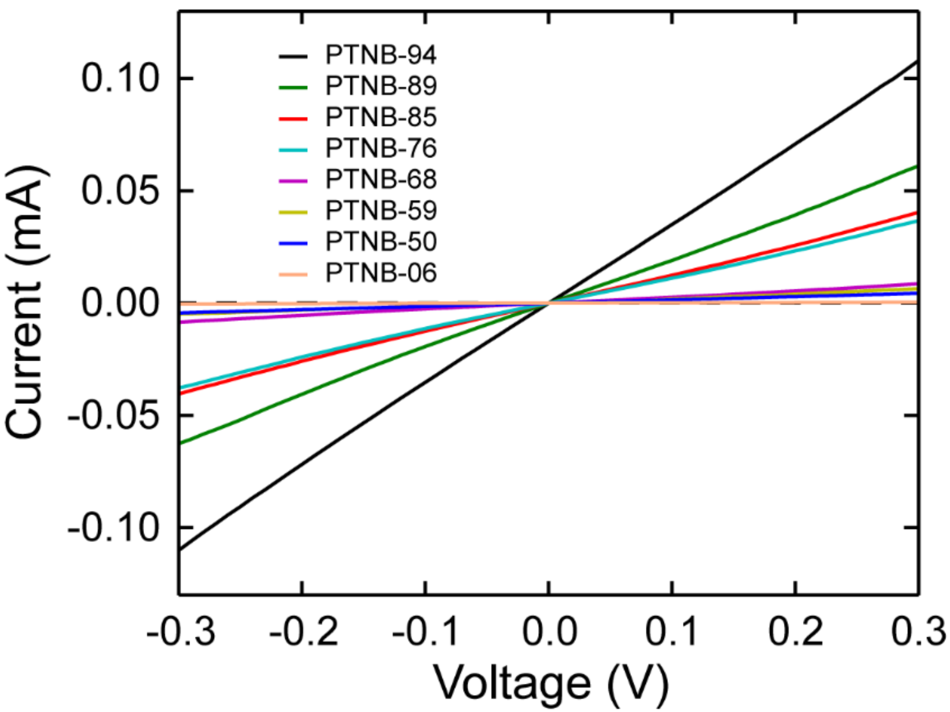


How Does Radical Density Affect Charge Transport?

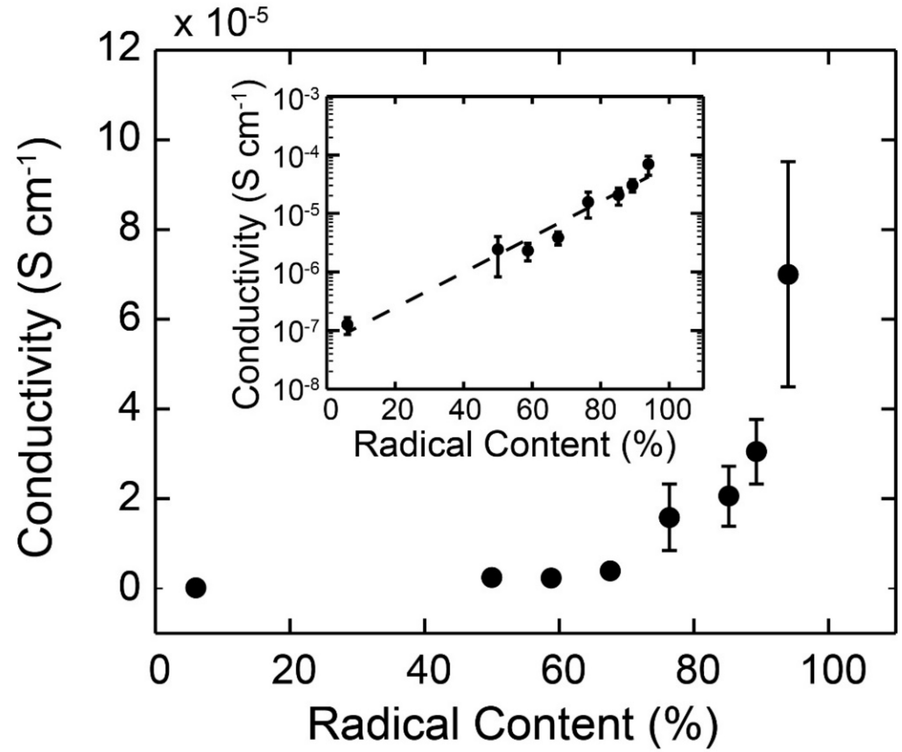
Hay, M. E.; Wong, S. H.; Mukherjee, S.; Boudouris, B. W. *J. Polym. Sci. Part B* **2017**, *55*, 1516-1525.

Conductivity Has an Exponential Dependence on Radical Content

Raw Current-Voltage Data For Different PTNB Loadings



Conductivity Depends Exponentially on Radical Density

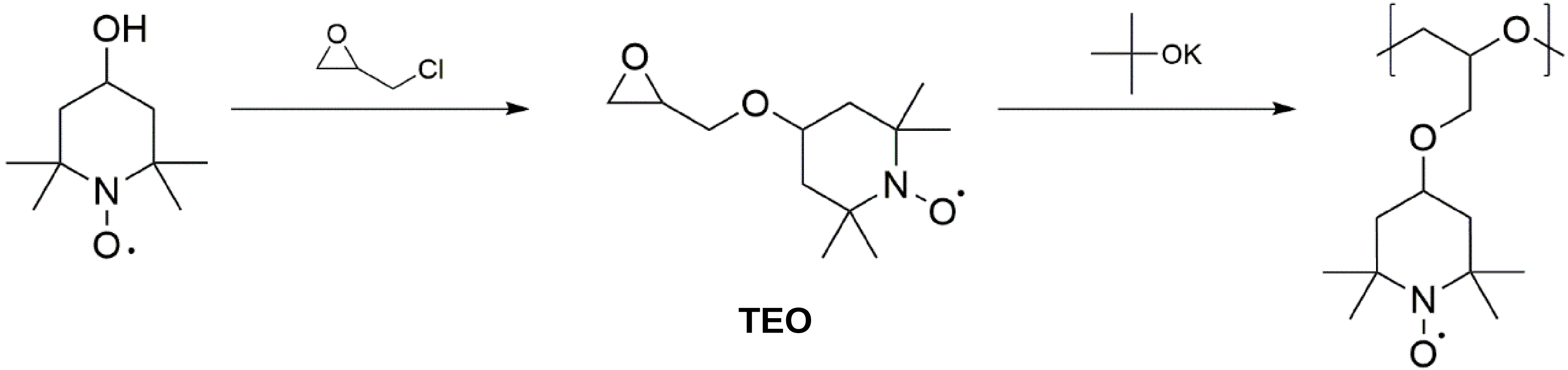


Key Radical Polymer Charge Transfer Points that Differ from Conjugated Polymers

1. Depends Strongly on Radical Density
2. Is Independent of Temperature below the Glass Transition Temperature of the Polymer

Hay, M. E.; Wong, S. H.; Mukherjee, S.; Boudouris, B. W. *J. Polym. Sci. Part B* **2017**, *55*, 1516-1525.

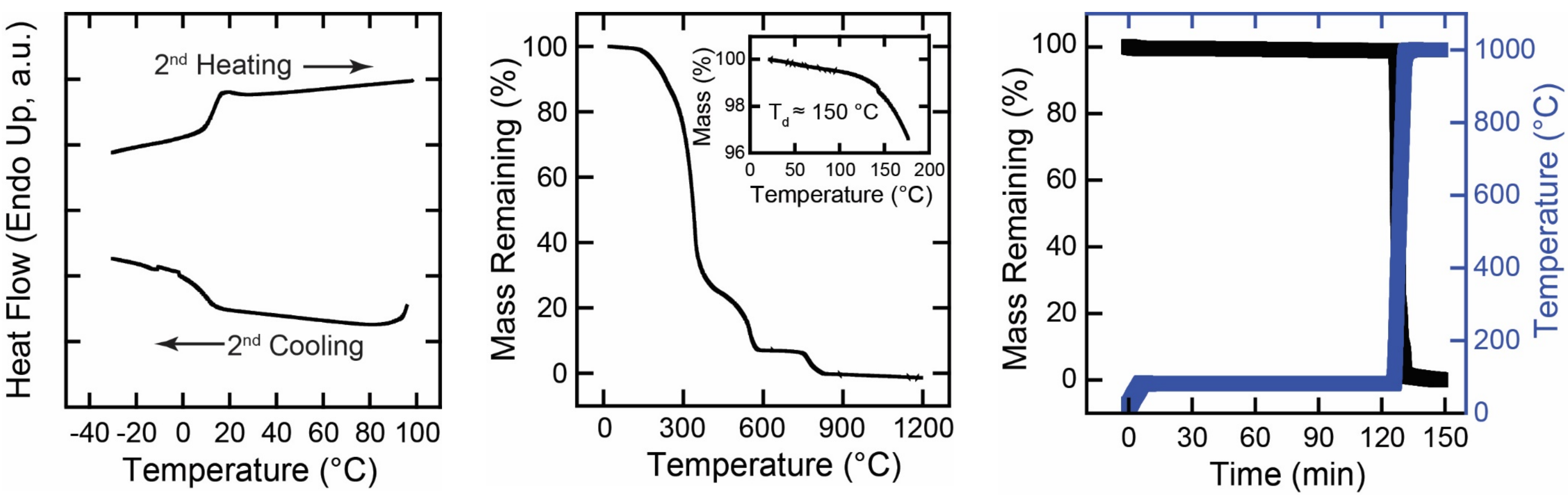
PTEO has Useful Thermal Transitions for a Radical Polymer



TEO

PTEO

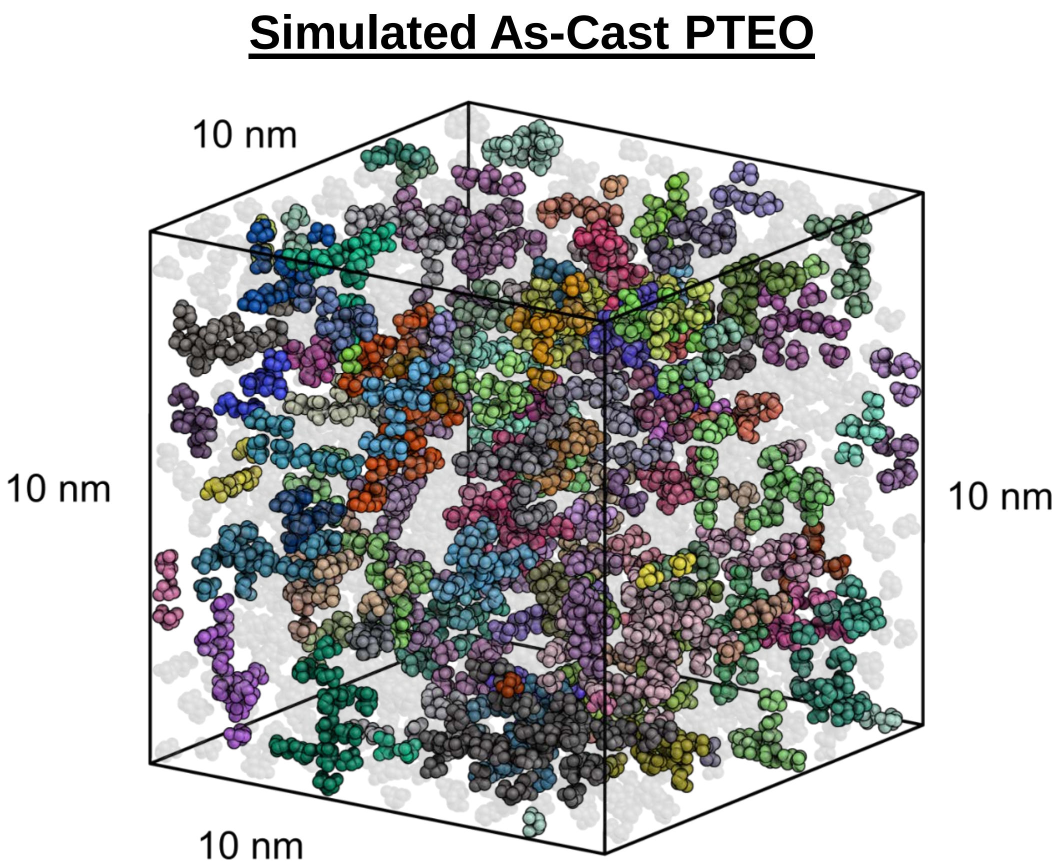
PTEO Has a T_g Much Lower than the Degradation Temperature

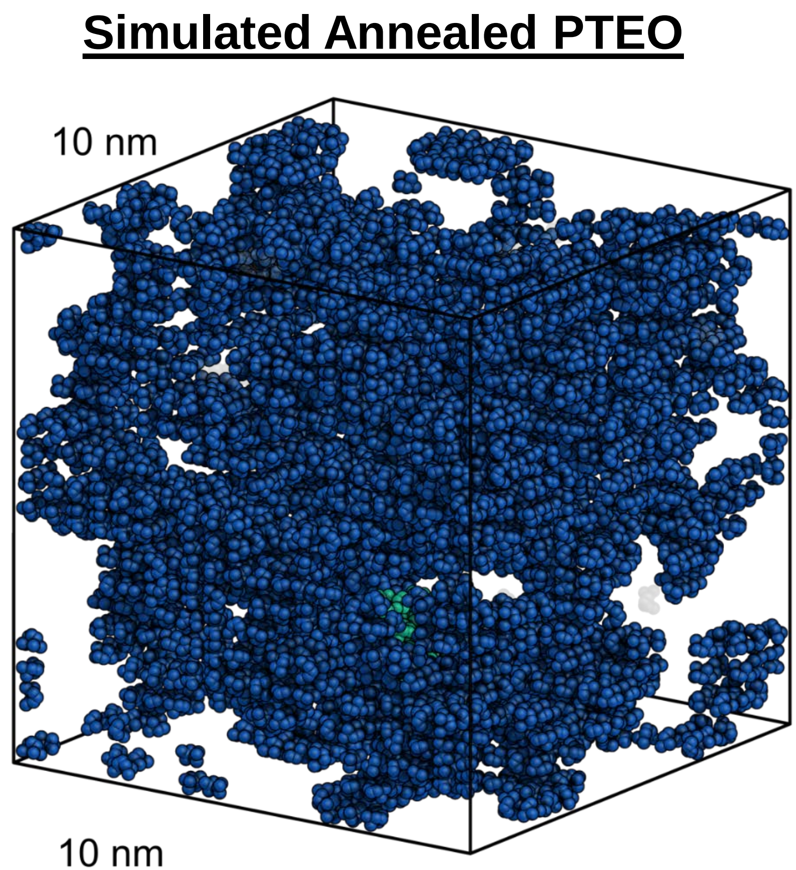


Joo, Y.; Agarkar, V.; Seung, S. H.; Savoie, B. M.; Boudouris, B. W. *Science* **2018**, *359*, 1391.

PTEO is the 1st Radical Polymer Able to Undergo Thermal Annealing

It is thermodynamically-favorable for the nitroxide groups to pair



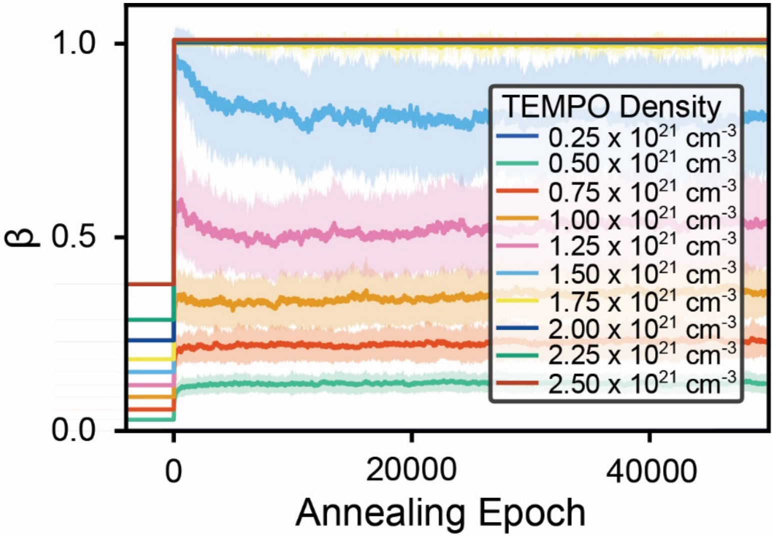


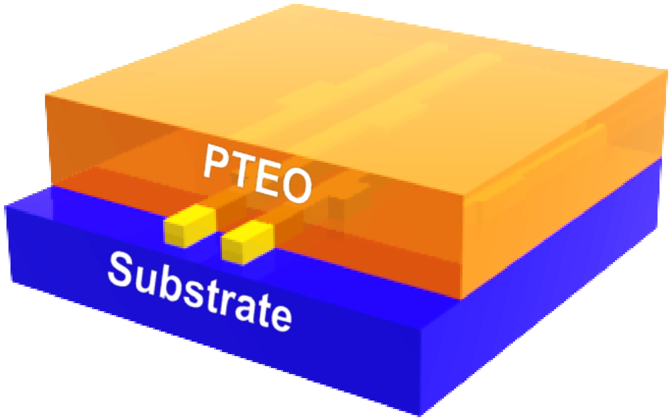
- Each color represents an isolated network of paired nitroxide groups.
- Any grayed groups are nitroxide groups that are not paired.

Joo, Y.; Agarkar, V.; Seung, S. H.; Savoie, B. M.; Boudouris, B. W. *Science* **2018**, *359*, 1391.

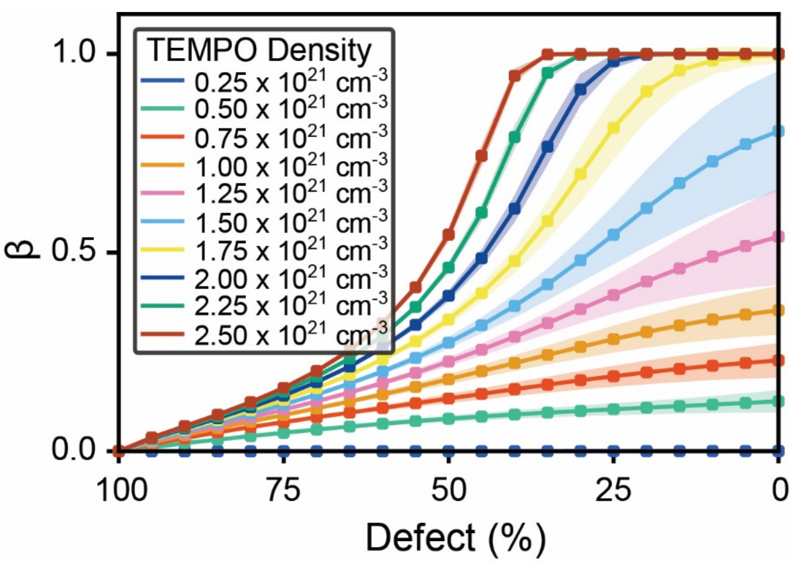
Annealing Shows Real-Time Percolation Path Formation

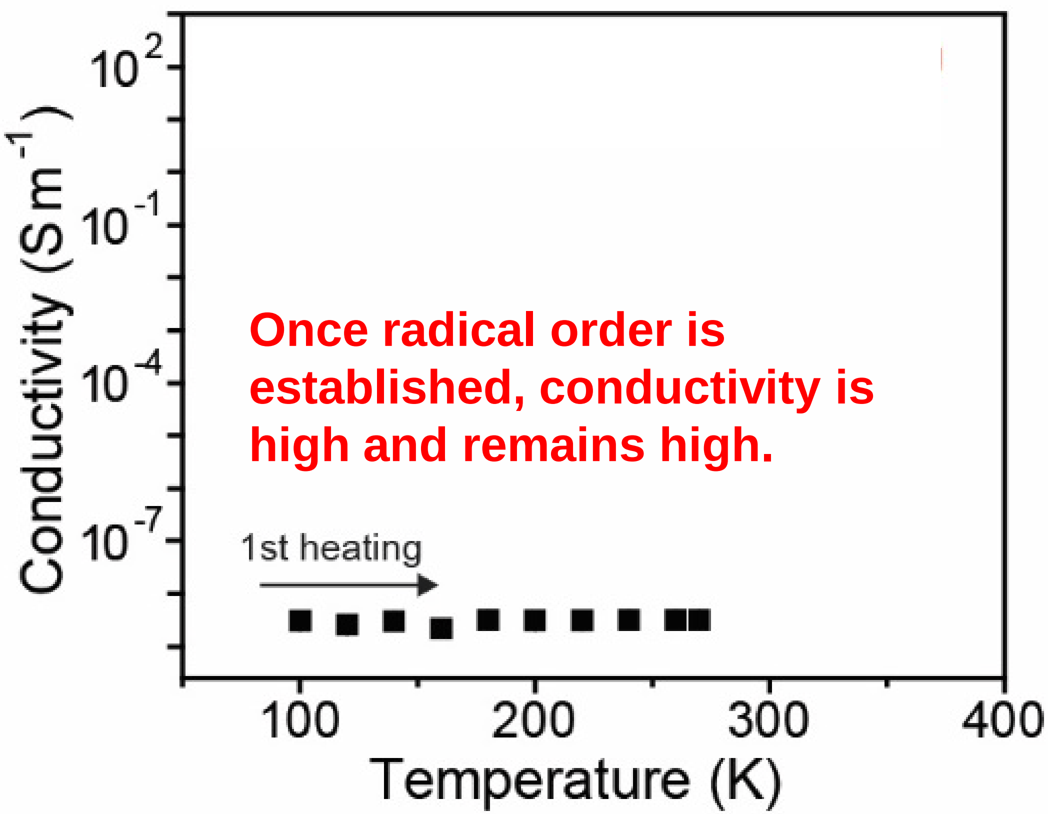
Predicted Annealing Trend





Predicted Defect Trend

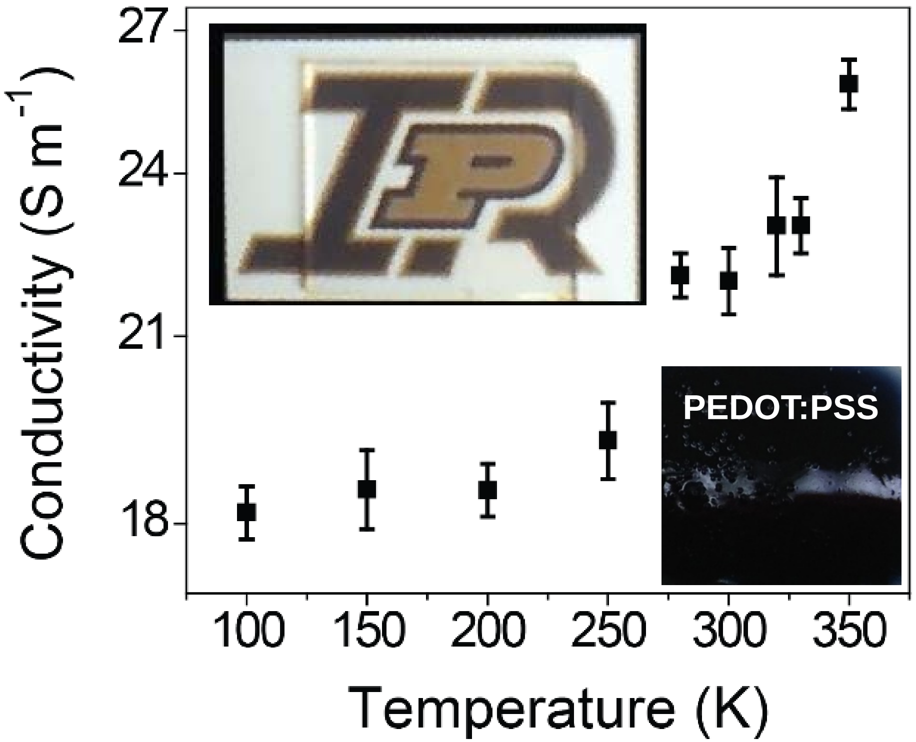




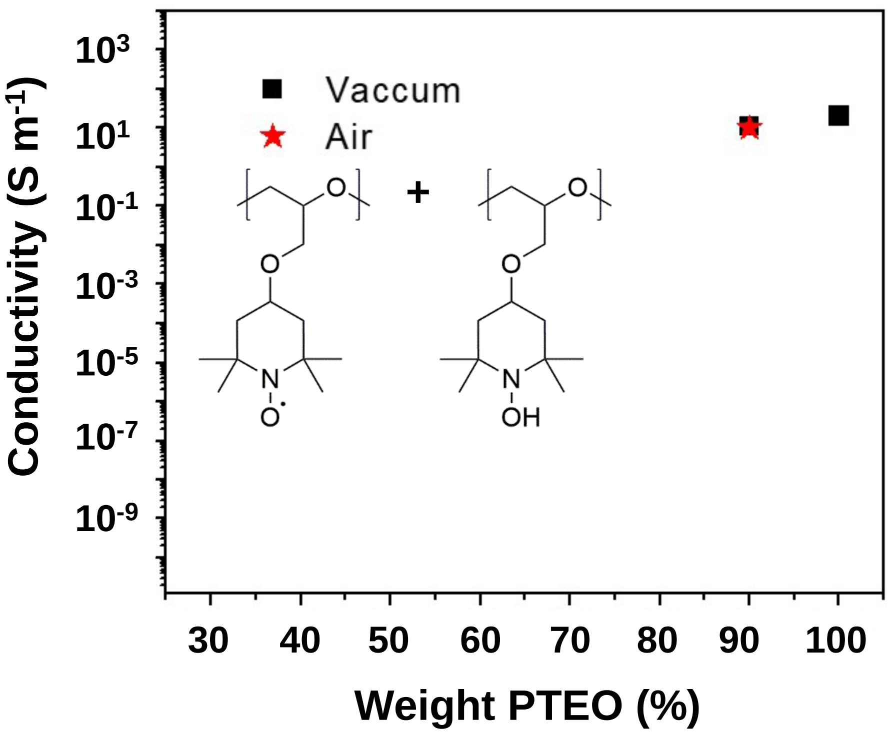
Once radical order is established, conductivity is high and remains high.

PTEO Has the Highest Conductivity of any Radical Polymer

Annealed PTEO Film



Radical Content is Critical



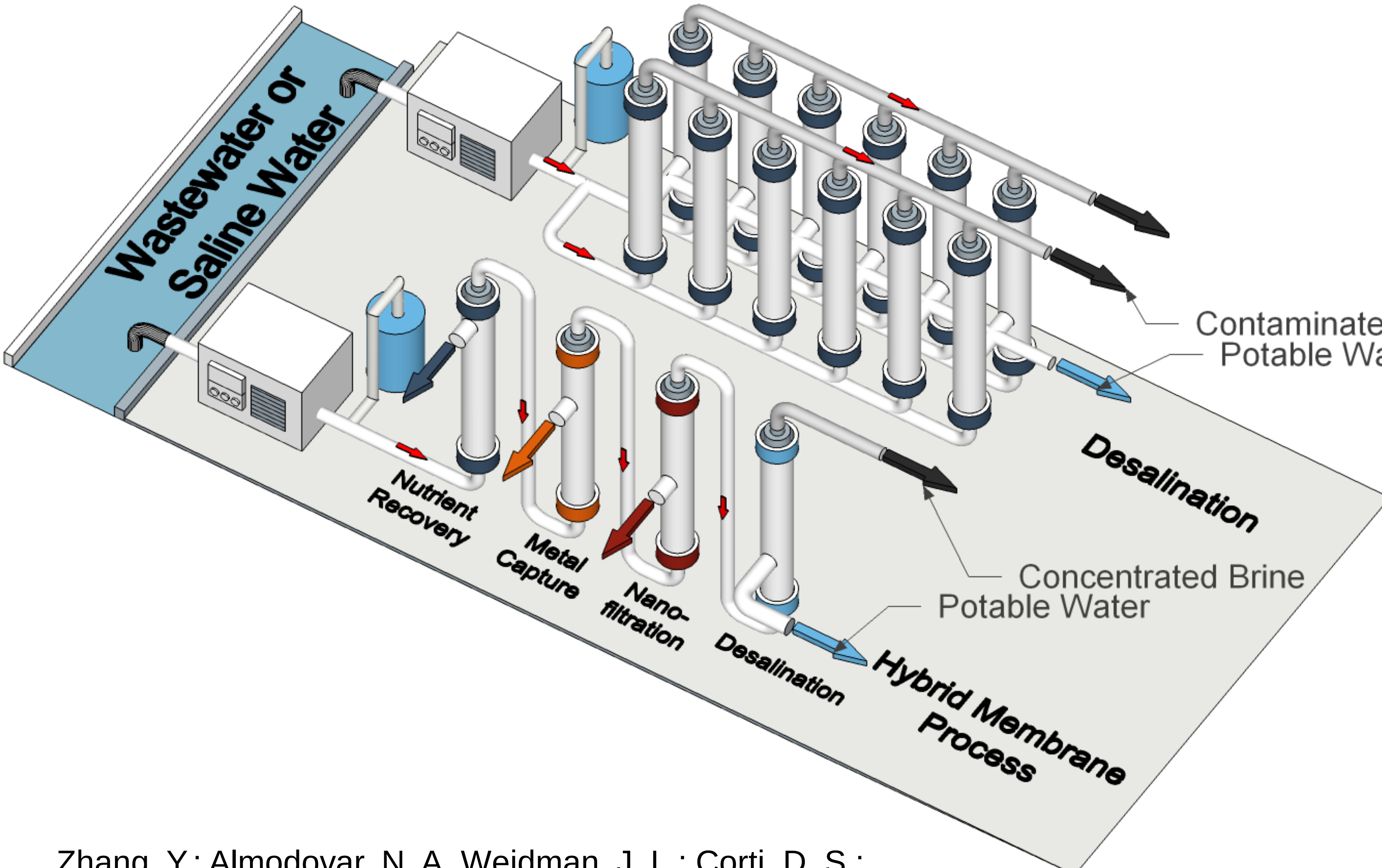
- If the film is annealed before testing, there is little change in conductivity.
- PTEO is a transparent conductor.

- The radical density within the thin film is critical for percolation to be reached.
- PTEO behaves the same in vacuum and in air.

Joo, Y.; Agarkar, V.; Seung, S. H.; Savoie, B. M.; Boudouris, B. W. *Science* **2018**, *359*, 1391.

Fit-for-Purpose Water is Critical to Future Global Success

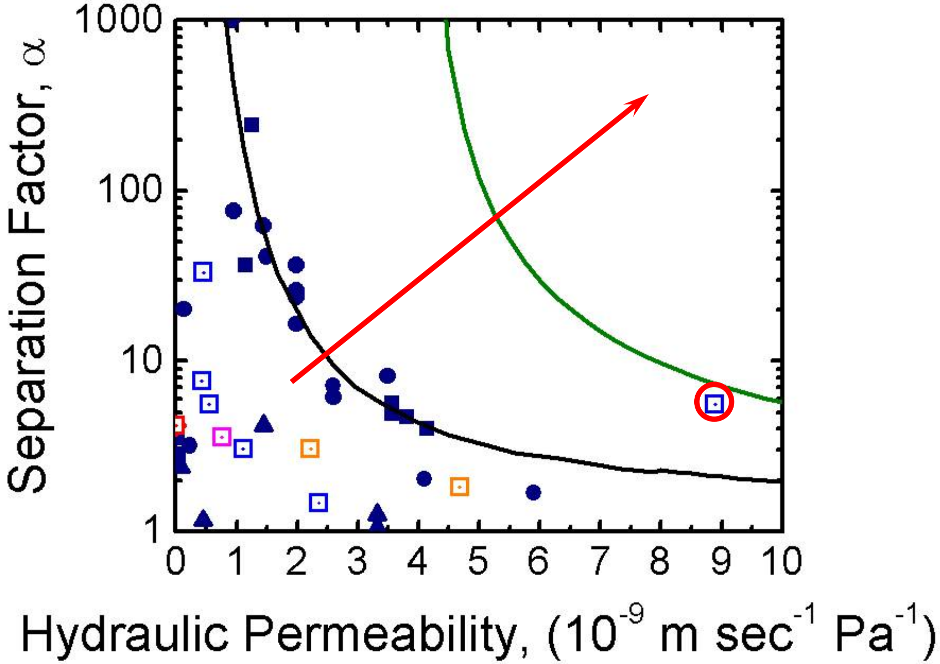
Contrasting Desalination Operations from Resource Recovery Trains



Zhang, Y.; Almodovar, N. A. Weidman, J. L.; Corti, D. S.; Boudouris, B. W.; Phillip, W. A. *npj Clean Water* **2018**, *1*, 2.

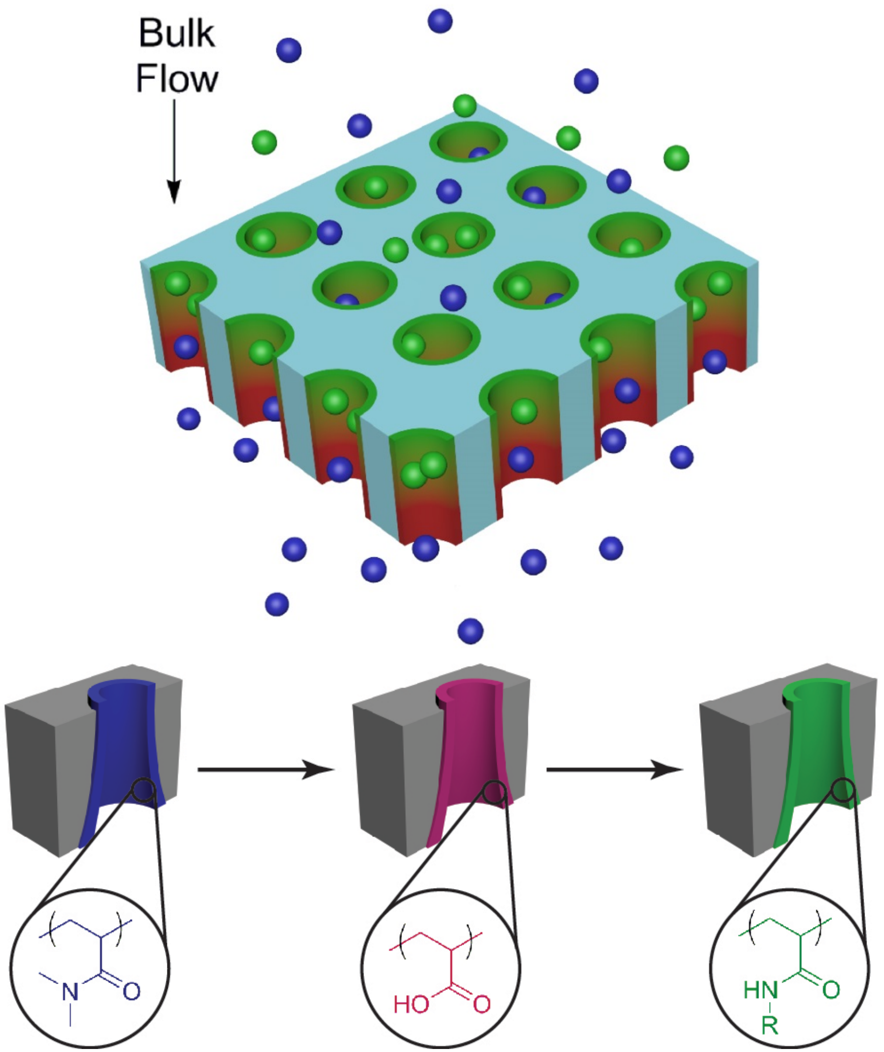
Nanoporous Materials for Filtration Applications

Robeson Plot of Commercial and Emerging Block Polymer-based Nanofiltration Membranes



Block Polymer-based Membranes Push the Limits of Traditional Materials Because of Their Ability to Have a High Density of Uniform Pore Sizes Across Large Areas

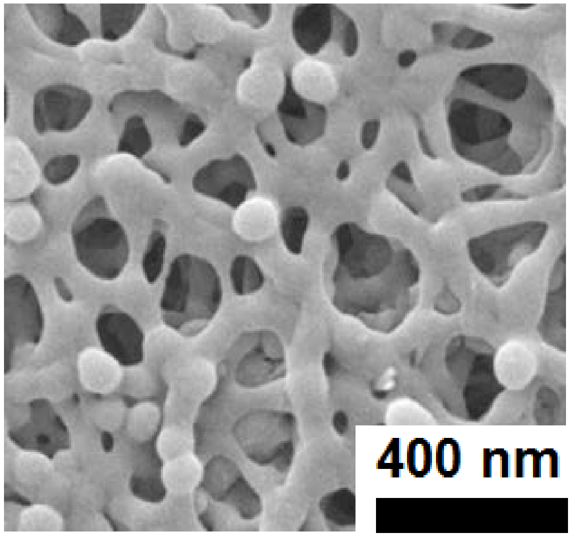
Functional Macromolecules Allow for Size AND Chemical Selectivity



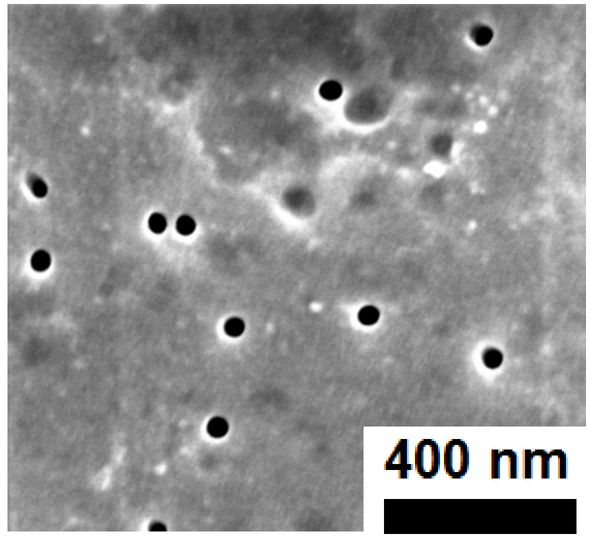
Zhang, Y.; Sargent, J. L.; Boudouris, B. W.; Phillip, W. A. *J. Appl. Polym. Sci.* **2015**, *132*, 41683.

Block Polymers Lead to High Flux and High Selectivity Membranes

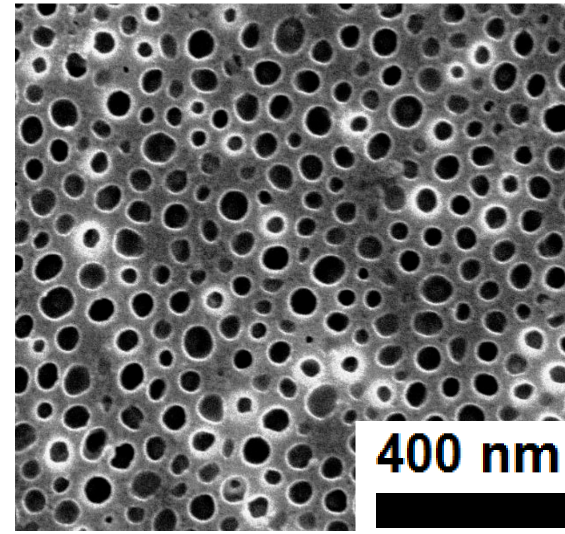
Phase Inversion



Track-etched

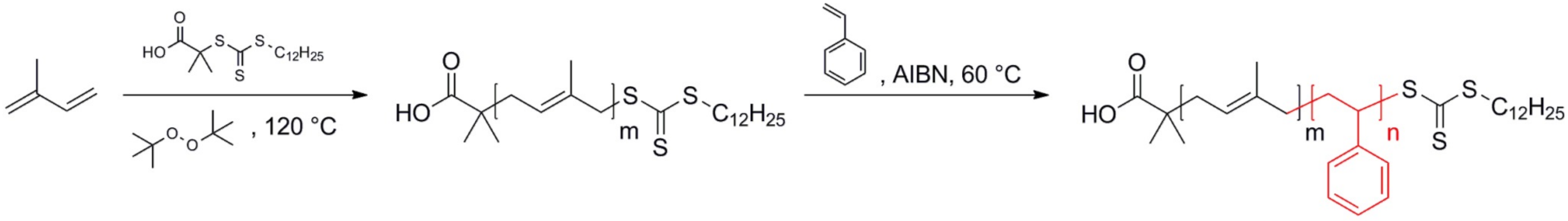


Self-assembled

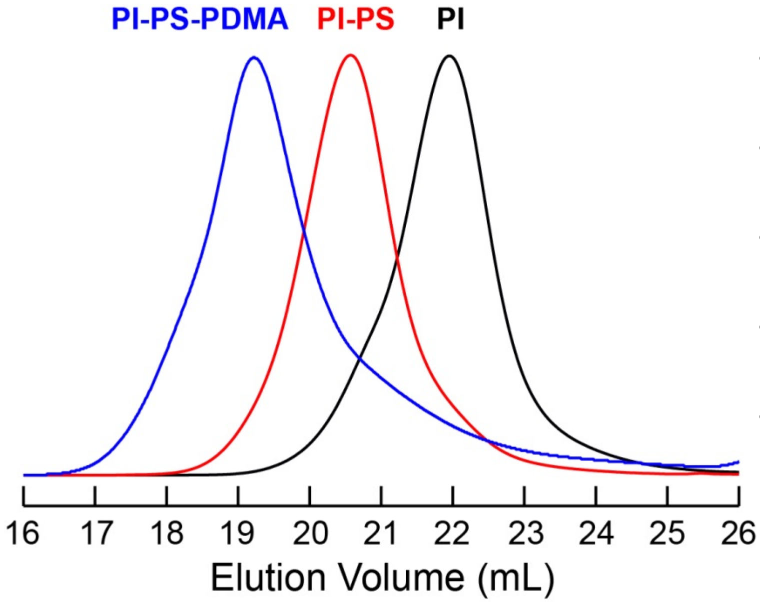


Self-assembly and Non-solvent Induced Phase Separation (SNIPS) Casting

RAFT Polymerization Generates Well-Defined Block Polymers



PI **PI-PS**

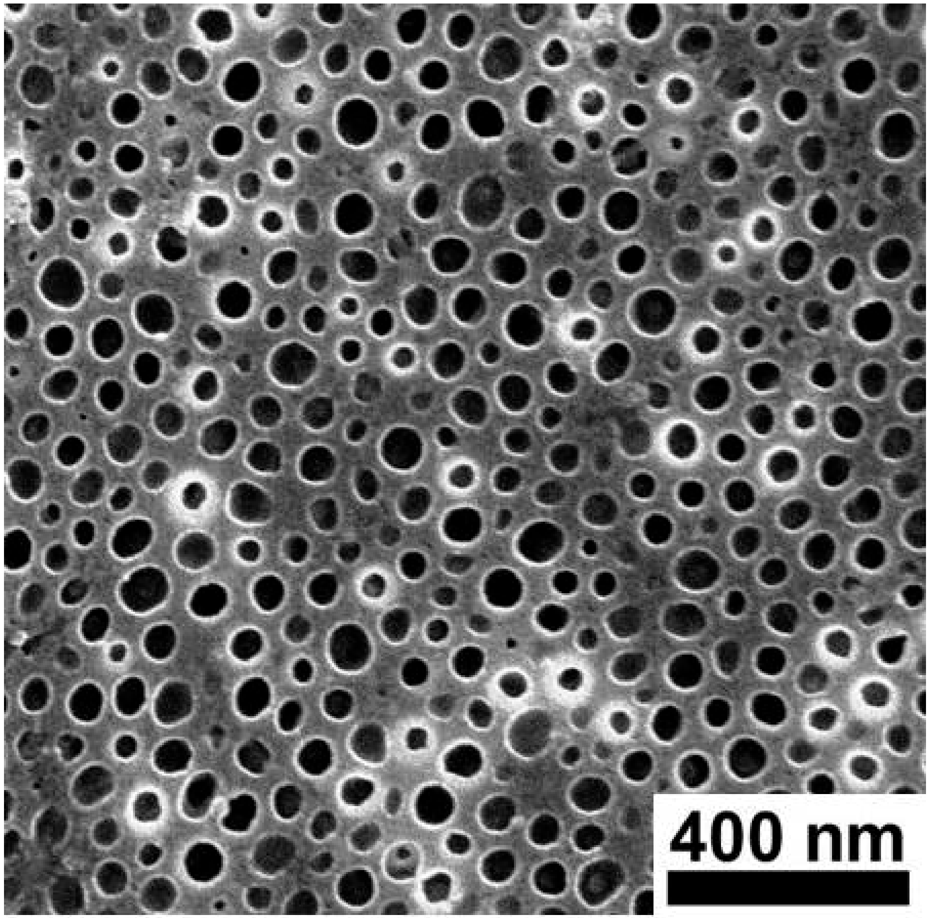


- **Tunable Molecular Weights (30 kg mol^{-1} < M_n < 150 kg mol^{-1})**
- **Narrow Molecular Weight Distributions (*Đ* ≤ 1.35)**
- **Powder Self-assembly: Hexagonally-Packed**
- **Key Parameter: PDMA Volume Fraction (f_{PDMA})**
- **For Self-assembly: 0.20 < f_{PDMA} < 0.25**

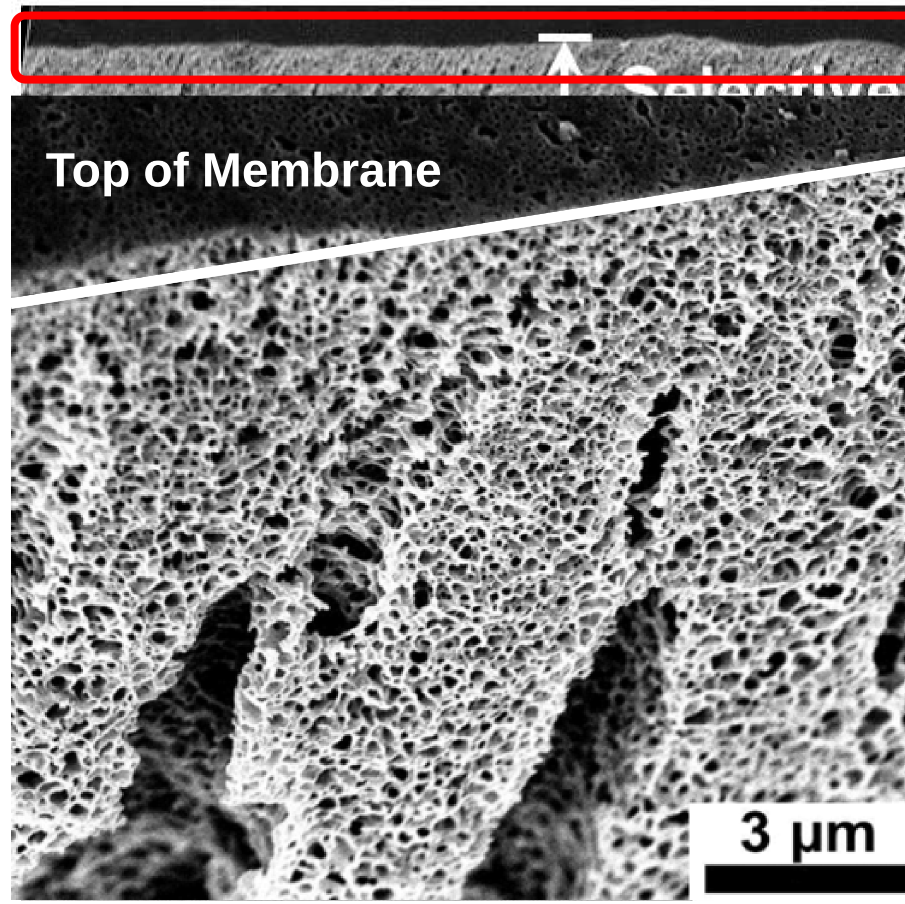
Mulvenna, R. A.; Prato, R. A.; Phillip, W. A.; Boudouris, B. W. *Macromol. Chem. Phys.* **2015,** *216*, 1831.

Tapered Nanostructure Leads to Thin Selective Layer

Top View of Membrane



Cross-Sectional View of Membrane

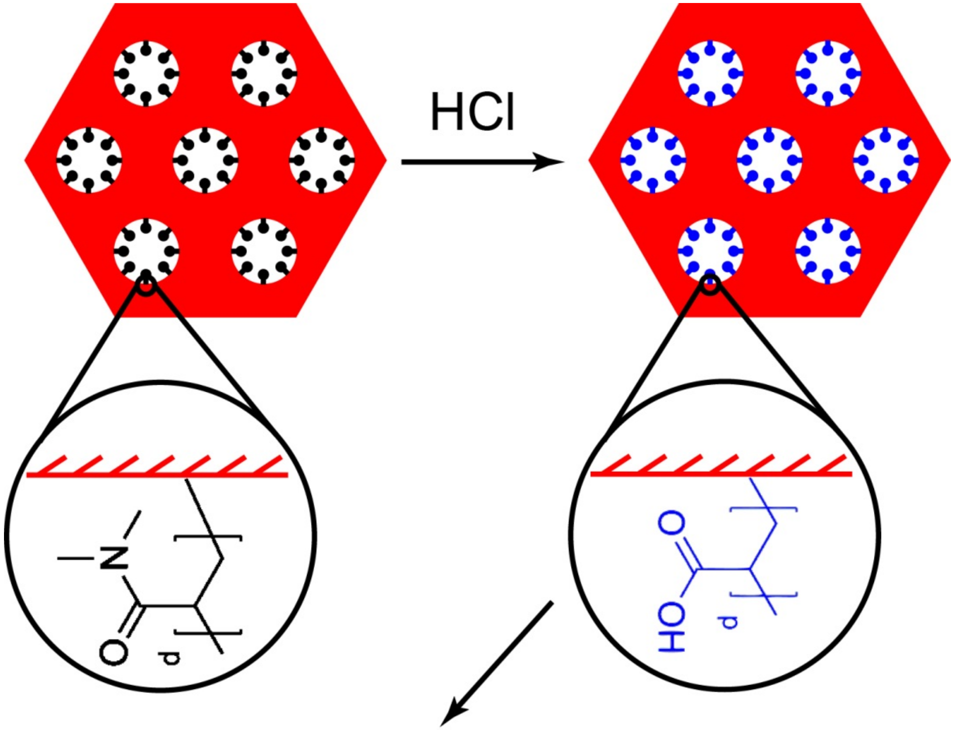


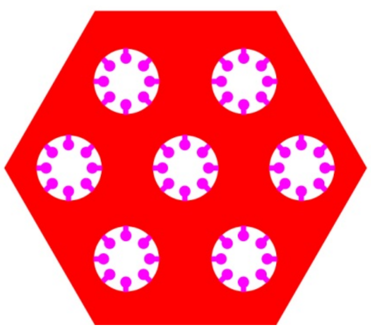
High Density of Pores at Surface: 9.4×10^{13} pores m^{-2}

Average Pore Size: 53 nm   20 nm in the dry state

Third Moiety (PDMA) Allows for Tunable Pore Chemistry

Solid State Reaction of Pore Lining



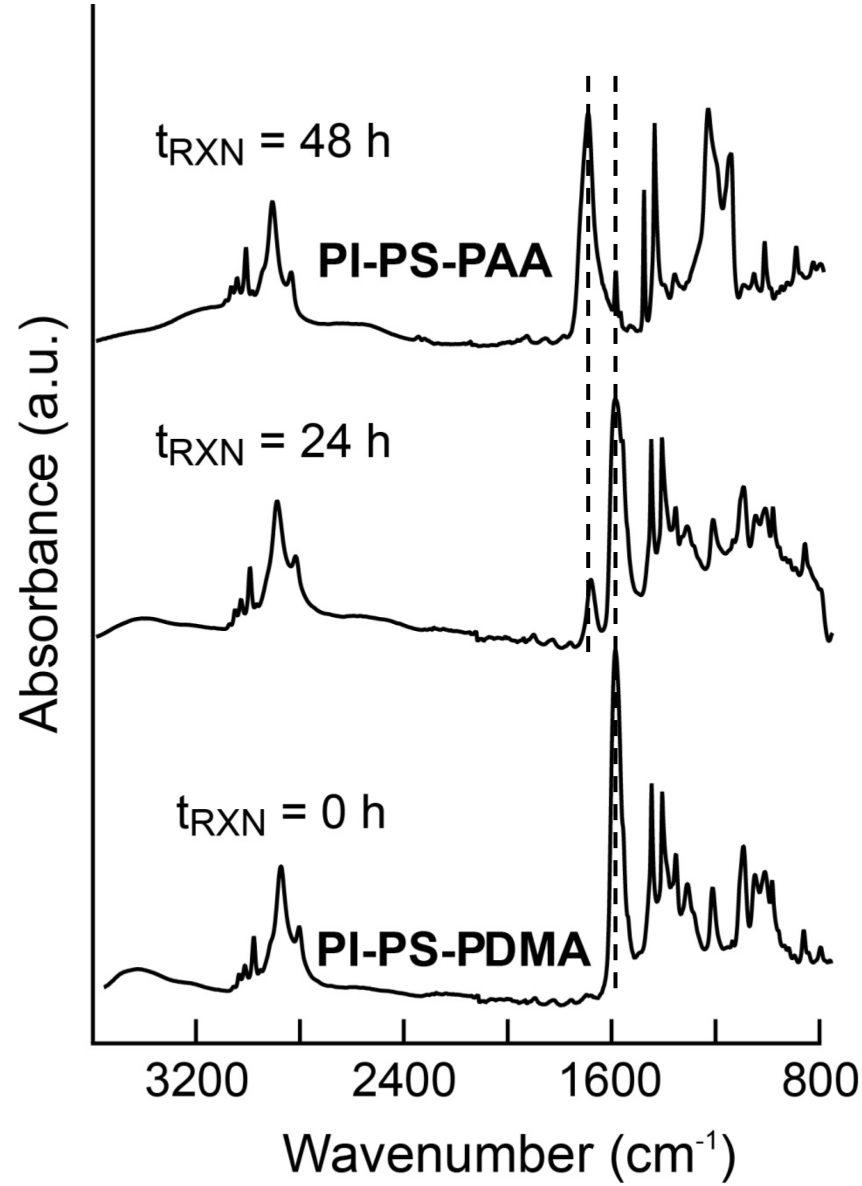


Chemistries Proven

- Thiols
- Amines
- Alkynes
- Alcohols

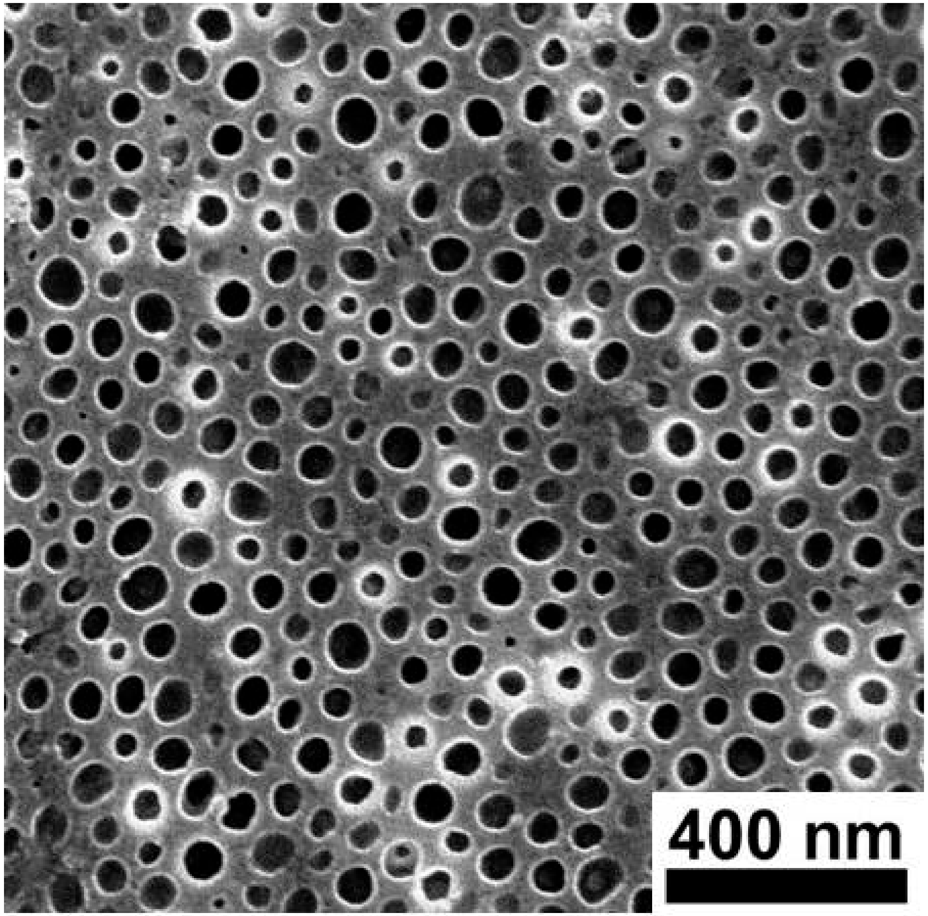
PAA Offers Robust Chemistry for Further Functionalization

Solid State Monitoring

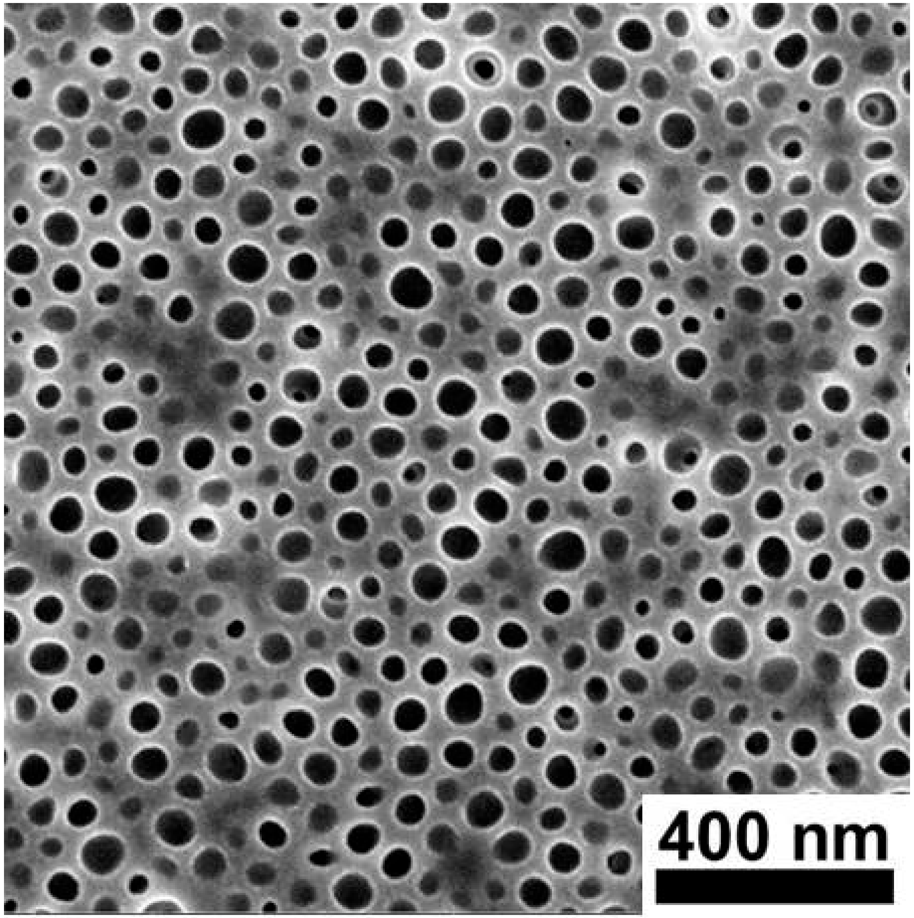


Change of Pore Chemistry Does Not Affect Nanostructure

<u>Before Deprotection Step</u>



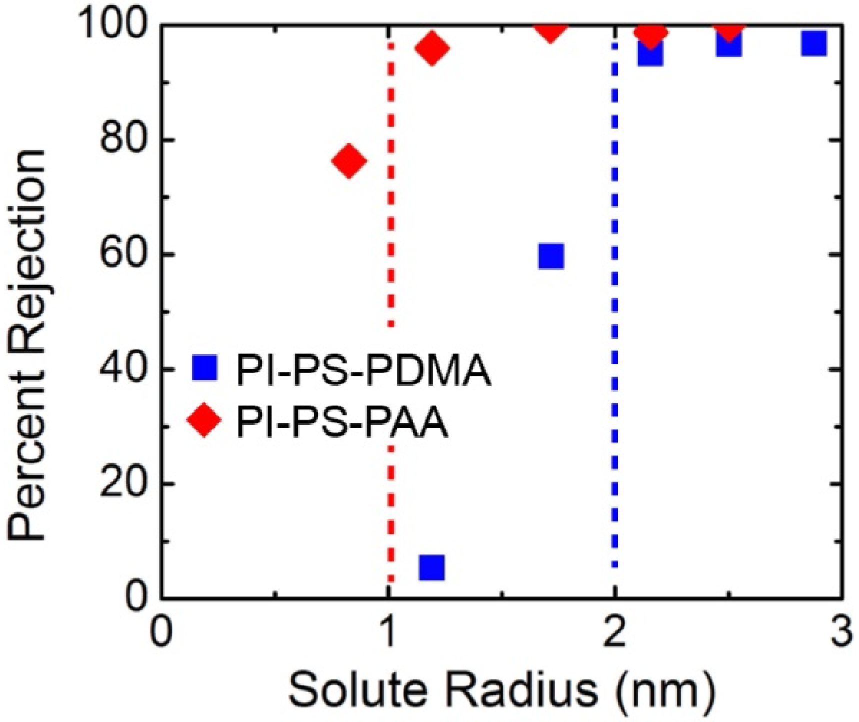
<u>After Deprotection Step</u>



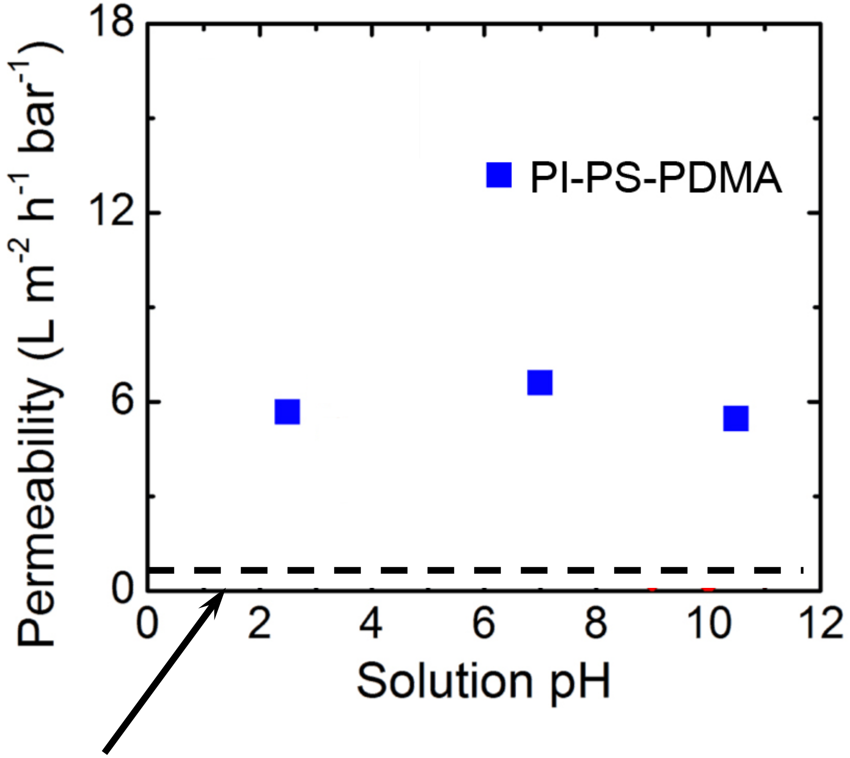
Less Than a 4% Difference in Microscopy-Measured Average Pore Size

Nanostructure Allows for High Flux and High Selectivity

Pore Sizes Down to Radii = 1 nm



pH-Dependent Fluxes



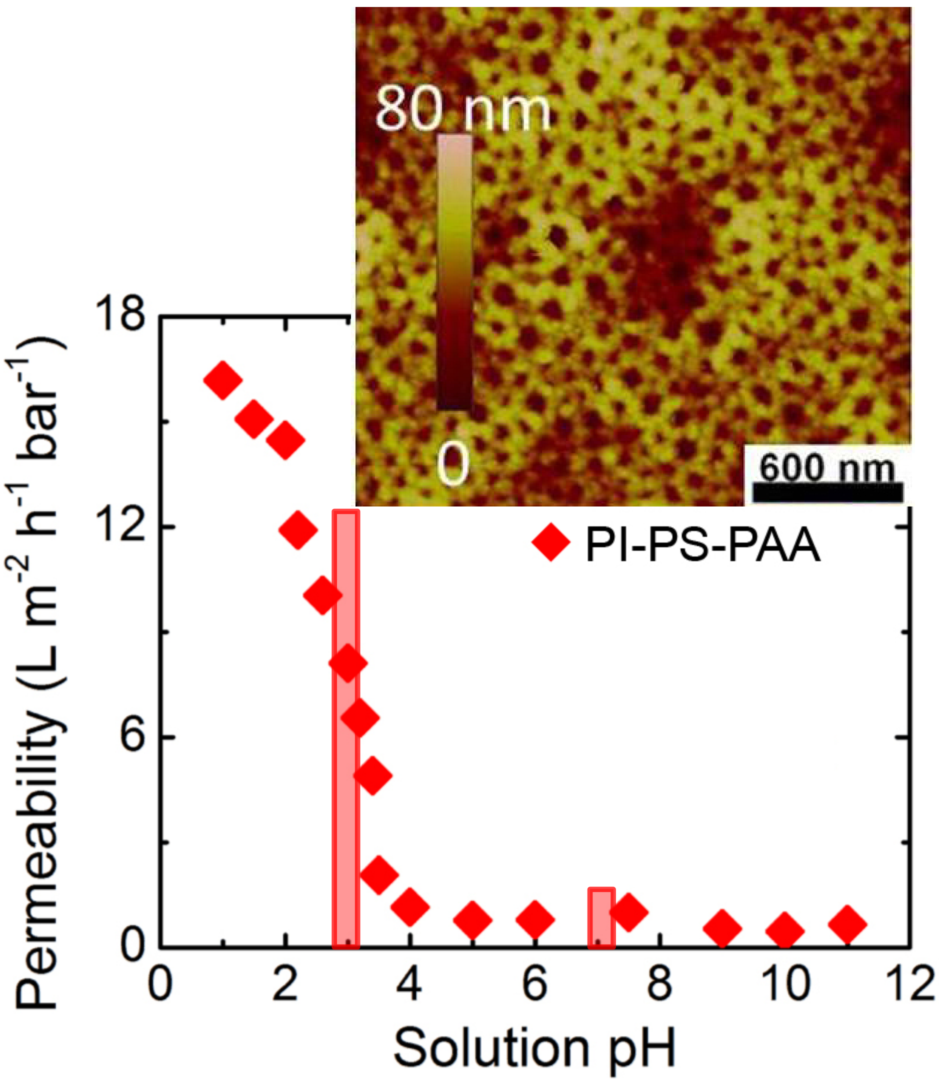
Typical RO Permeability for Commercial Membranes

Pore Changes Because of PAA Chemistry and Chain Rearrangement

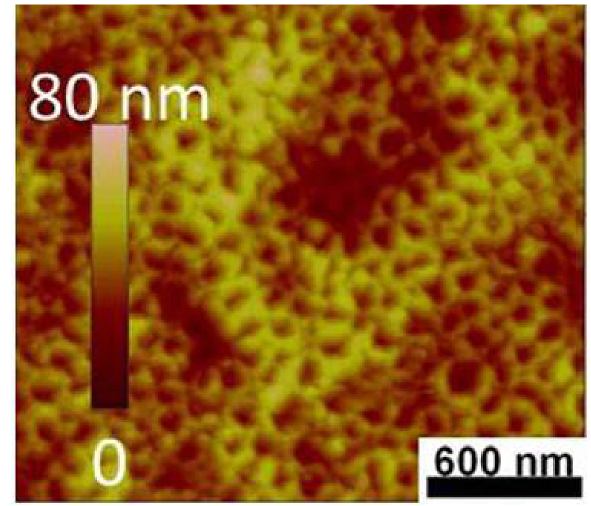
Mulvenna, R. A.; Weidman, J. L.; Jing, B.; Pople, J. A.; Zhu, Y.; Boudouris, B. W.; Phillip, W. A. *J. Membr. Sci.* **2014,** *470*, 246.

Environmental Microscopy Images Pore Diameter Changes

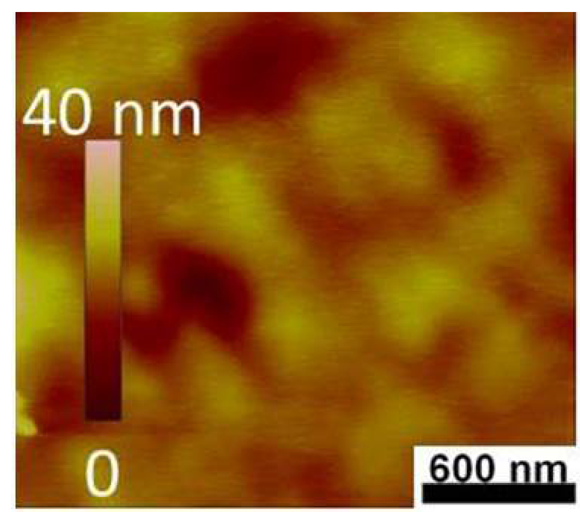
Dry PI-PS-PAA Membrane



Solution pH = 2.98

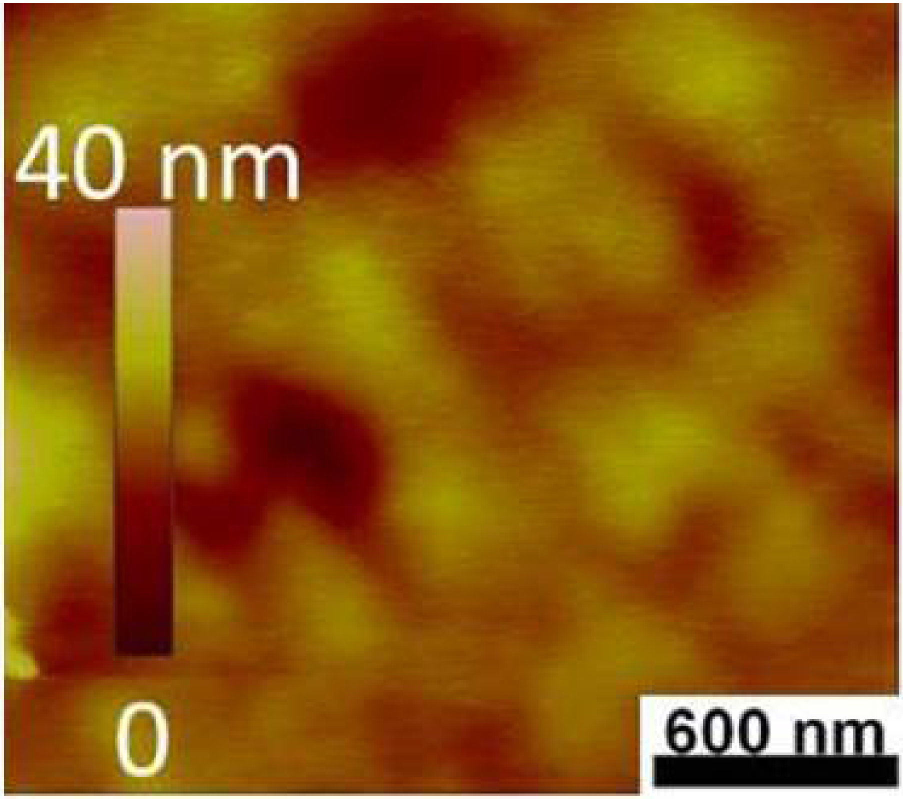


Solution pH = 6.88

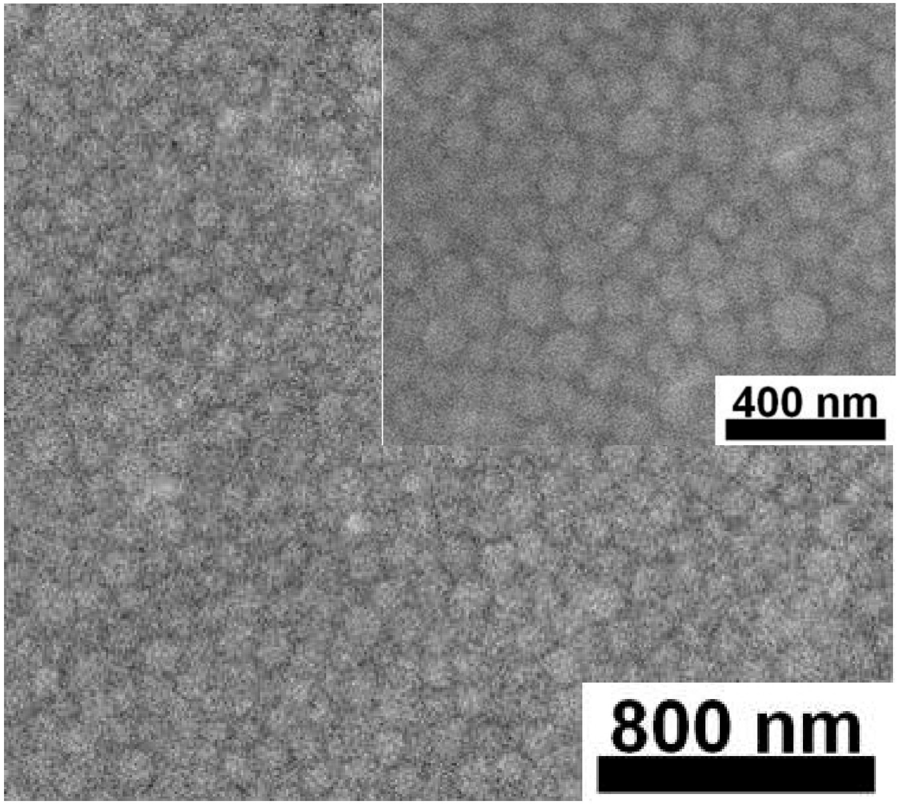


Environmental Microscopy Images Pore Diameter Changes

AFM Image at pH = 6.88 Solution



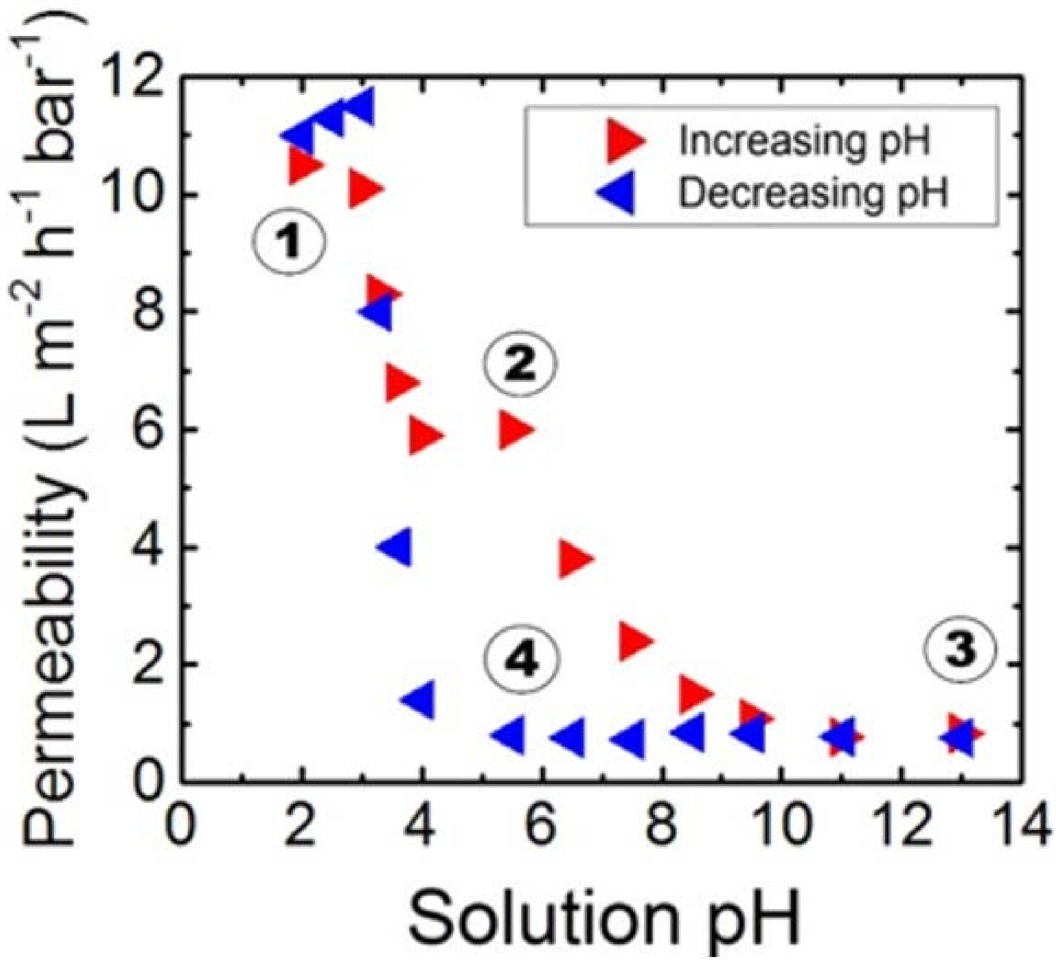
SEM Image with Ionic Liquid



This Pore Diameter Change is Complicated, and It is the Result of Many Intermolecular Interactions in Confined Geometries

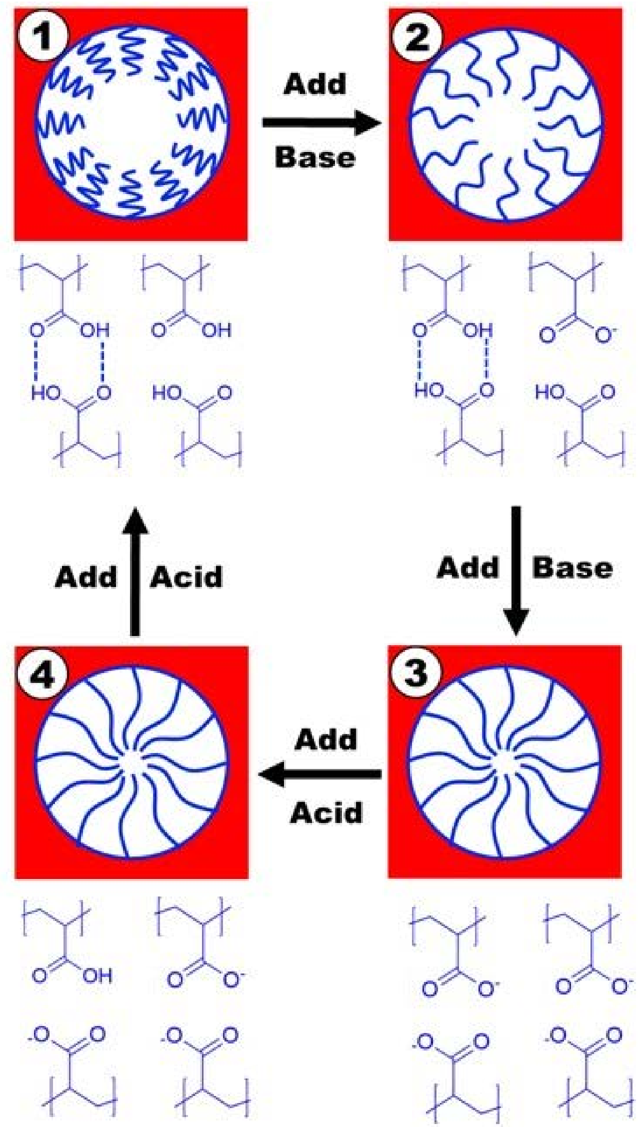
There is Flux Hysteresis as a Function of Solution pH

Path-Dependent, pH-Dependent Membrane Flux Properties

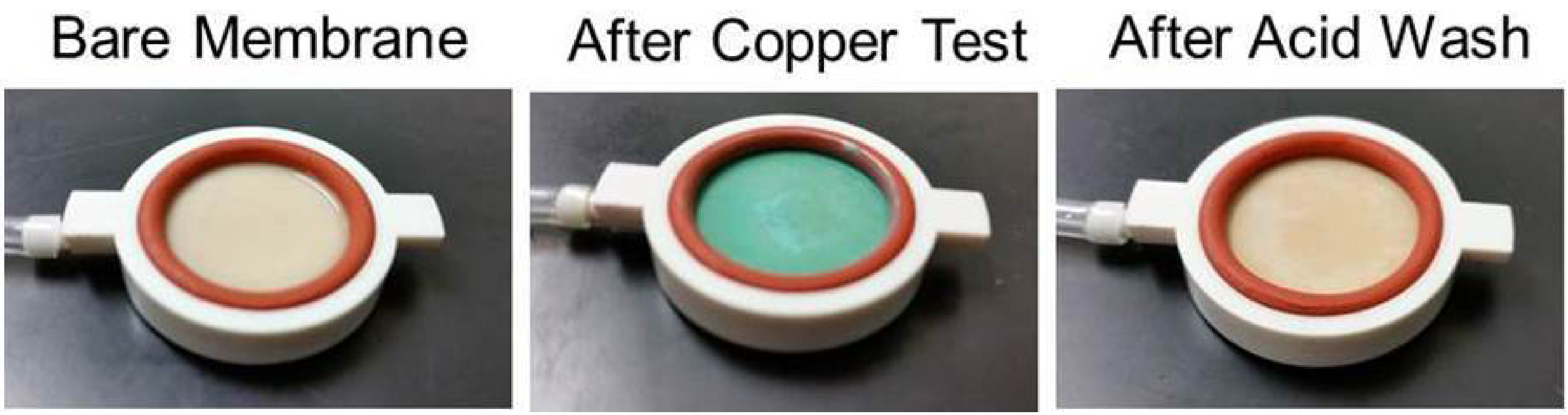


Weidman, J. L.; Mulvenna, R. A.; Boudouris, B. W.; Phillip, W. A. *J. Am. Chem. Soc.* **2016**, *138*, 7030-7093.

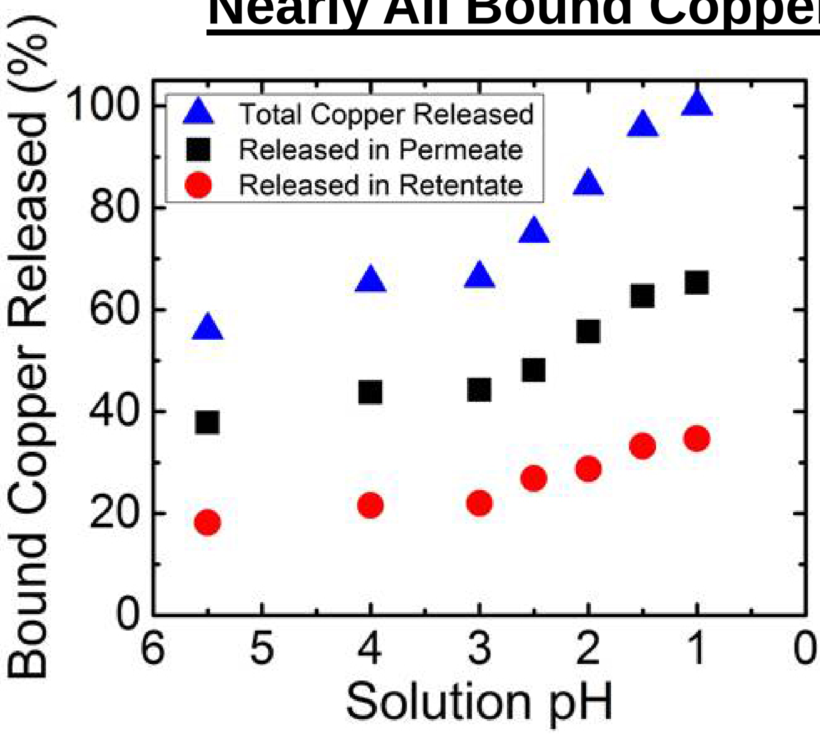
H-Bonding Interactions

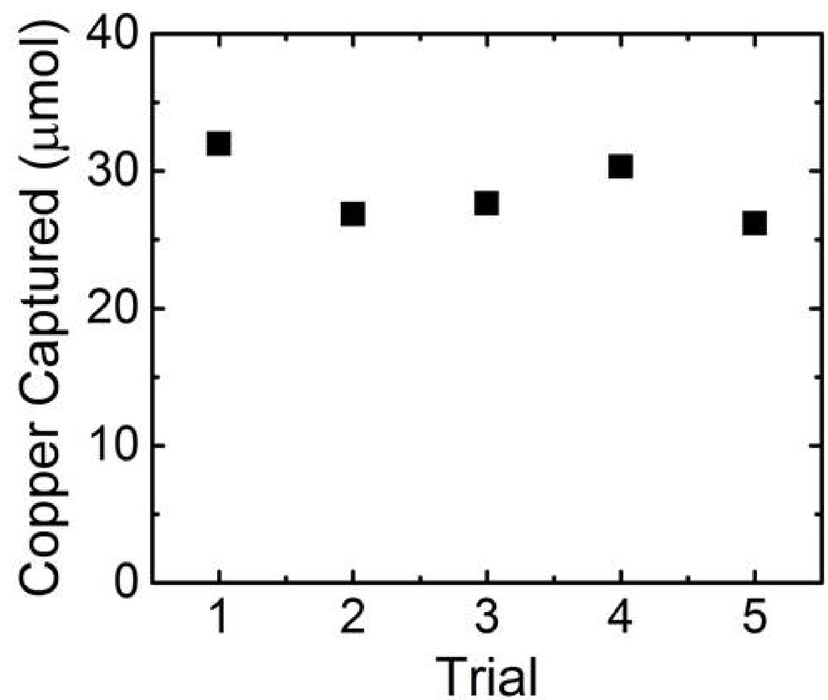


Cu^{2+} Binding is Reversible; Allows for Multiple Cycles



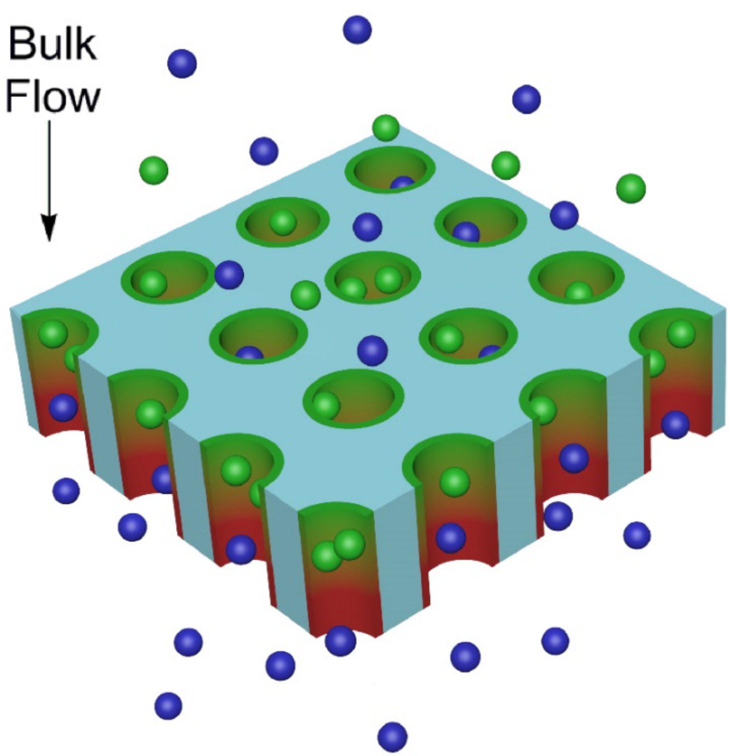
Nearly All Bound Copper is Released with an Acidic Wash



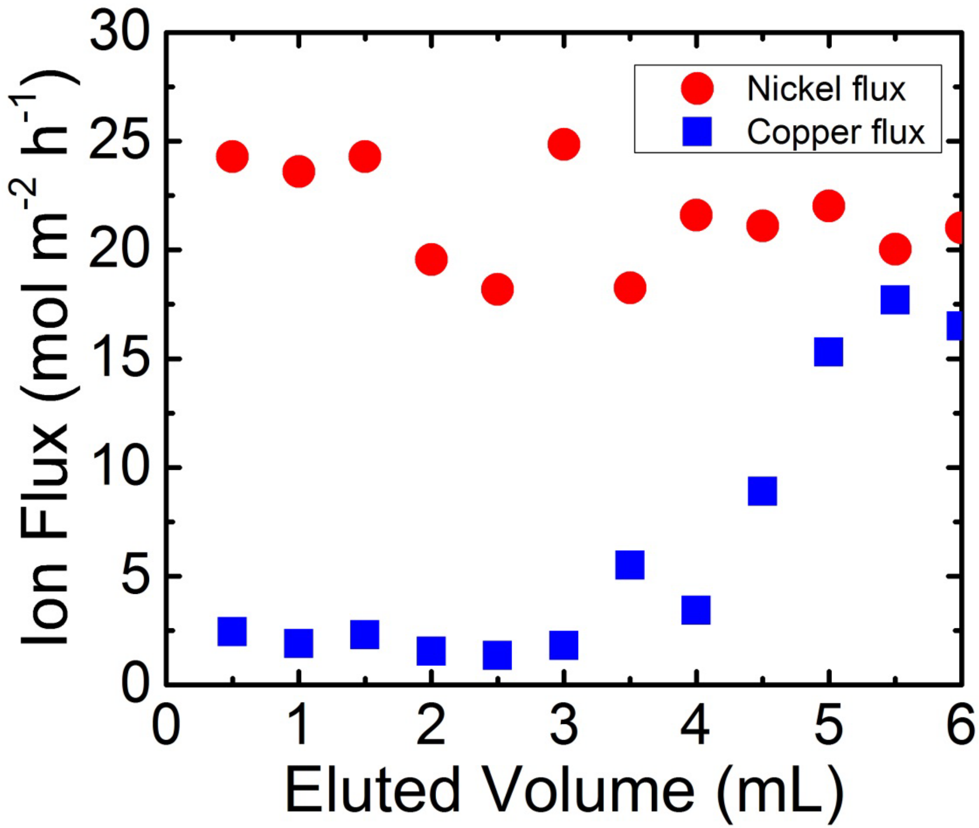


The PAA Pore Chemistry is Selective for Cu^{2+} over Ni^{2+}

Size AND Chemical Selectivity



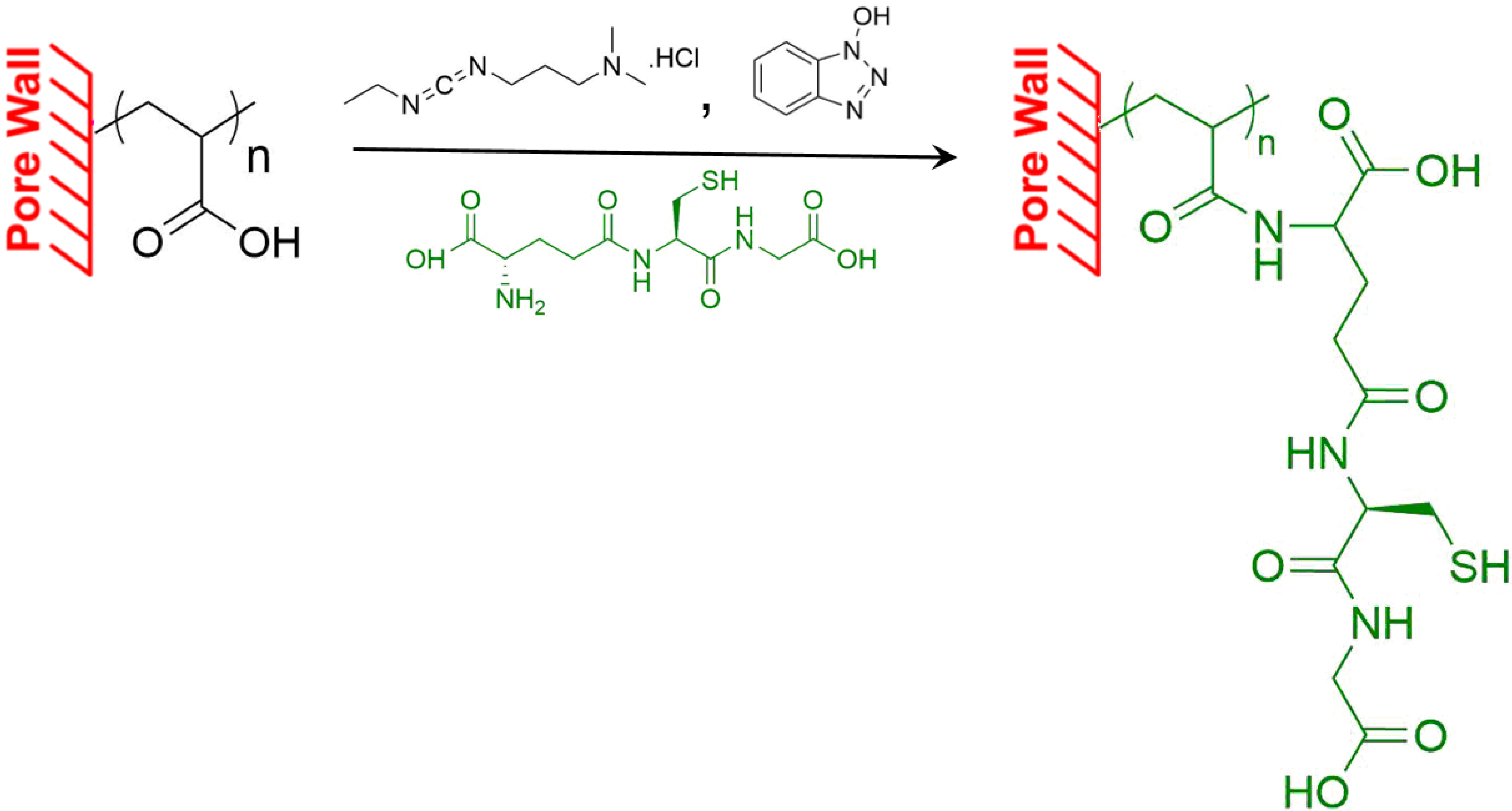
Separating Metal Ions



14:1 Cu^{2+}:Ni^{2+} Selectivity Until Breakthrough Occurs in the Membrane

Weidman, J. L.; Mulvenna, R. A.; Boudouris, B. W.; Phillip, W. A. *Langmuir* **2015,** *31*, 11113-11123.

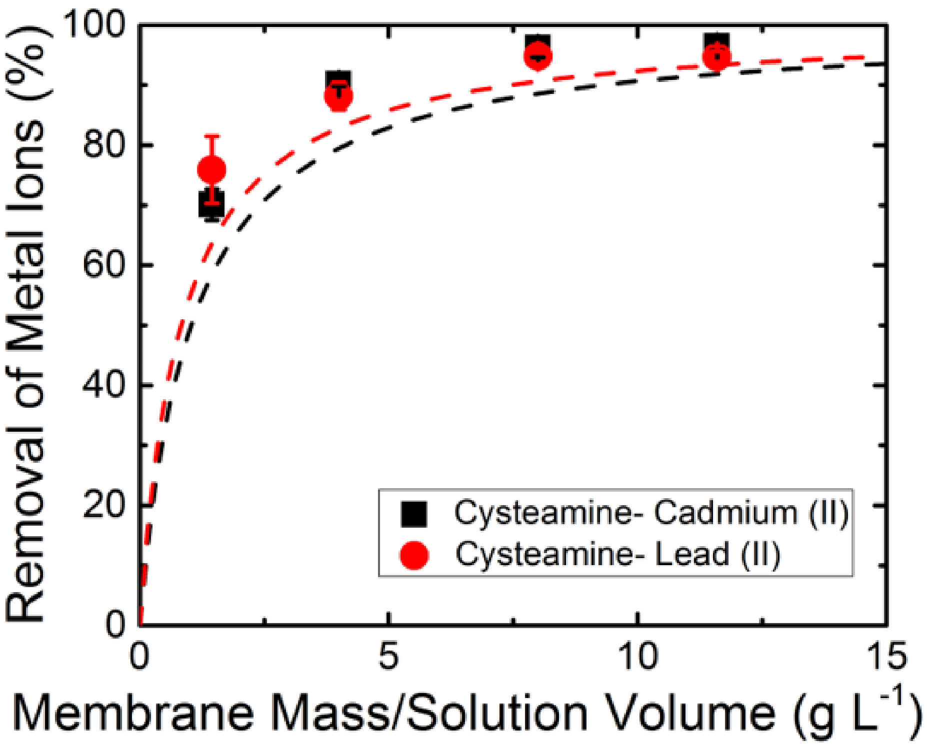
Bio-Inspired Groups Bind Cd^{2+} and Pb^{2+} Ions Very Well



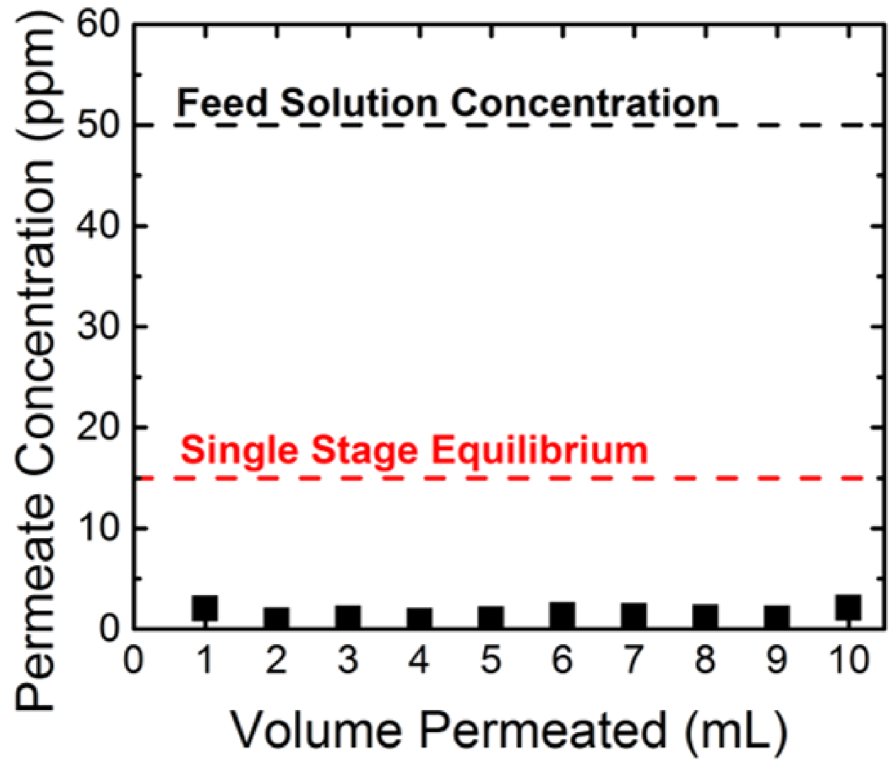
Weidman, J. L.; Mulvenna, R. A.; Boudouris, B. W.; Phillip, W. A. *ACS Appl. Mater. Interface*. **2017**, *9*, 19152-19160.

Chemistry and Nanostructure Lead to High Performance

Structure of the Membrane Allows for High Capacity



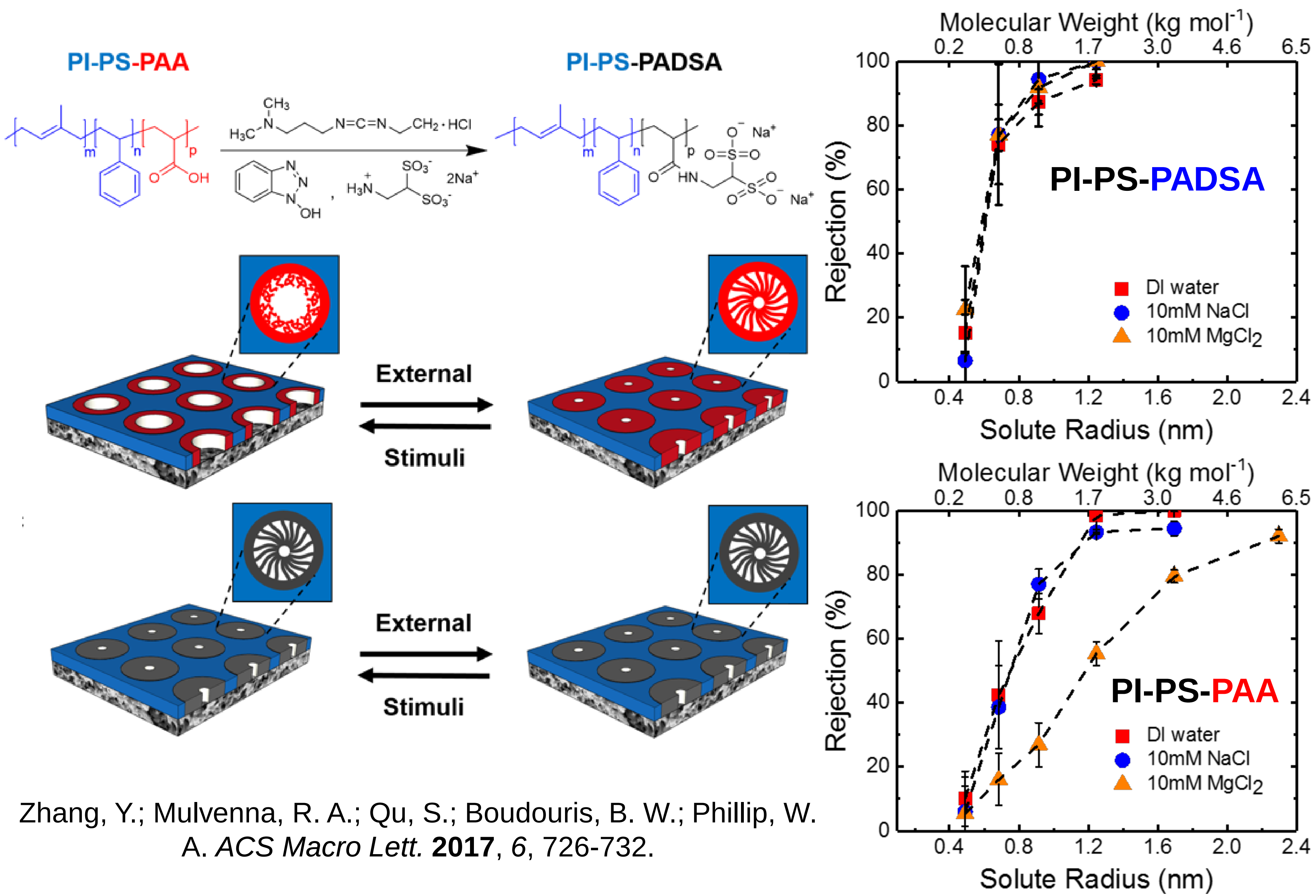
Tapered Structure Acts Like Multiple Stages



Membrane Adsorber Can Purify ~500 Times Its Own Weight in Water

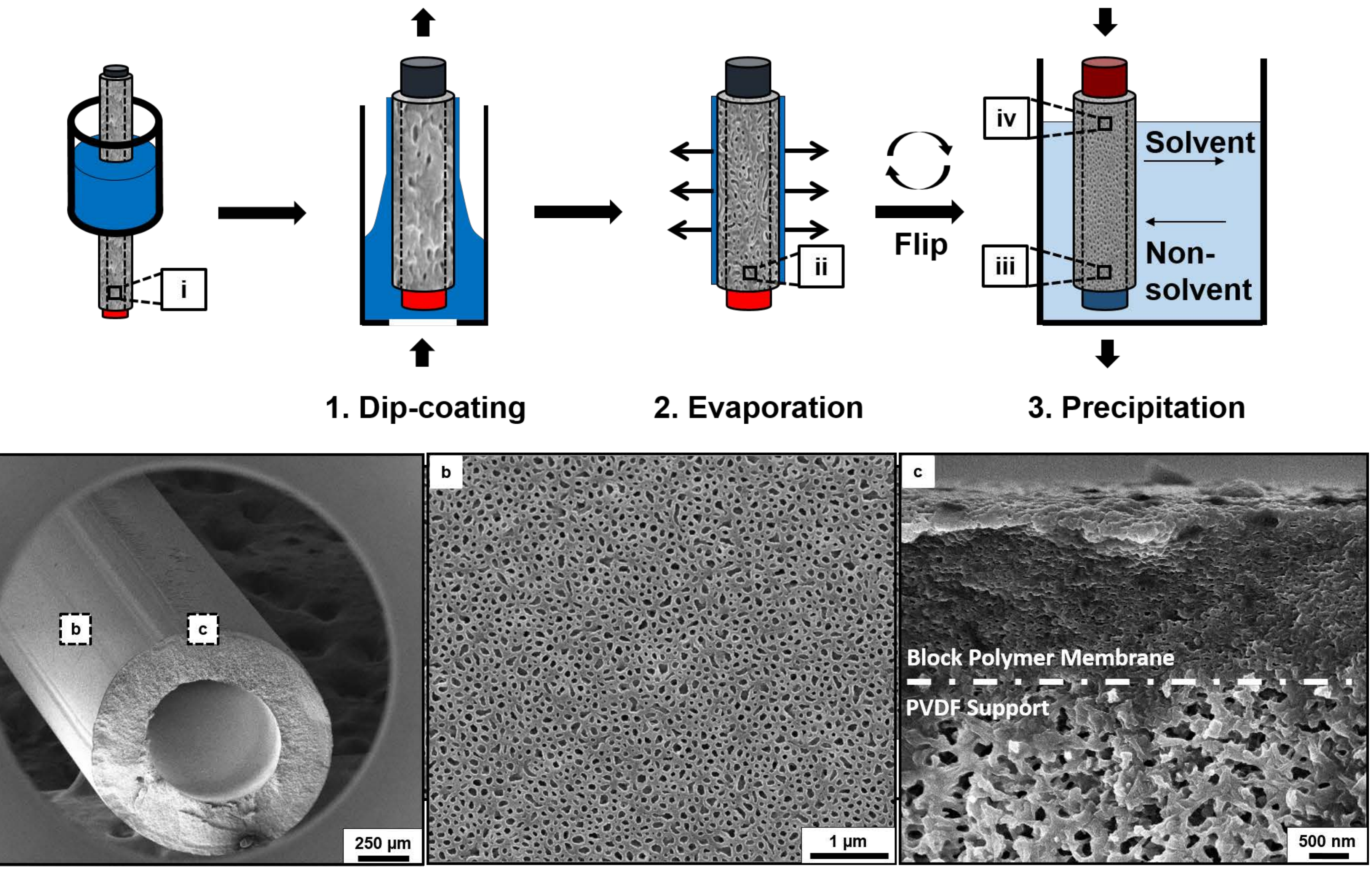
Weidman, J. L.; Mulvenna, R. A.; Boudouris, B. W.; Phillip, W. A. *ACS Appl. Mater. Interface*. **2017**, *9*, 19152-19160.

PADSA Allows for Wide Range of Operating Conditions



Zhang, Y.; Mulvenna, R. A.; Qu, S.; Boudouris, B. W.; Phillip, W. A. *ACS Macro Lett.* **2017**, *6*, 726-732.

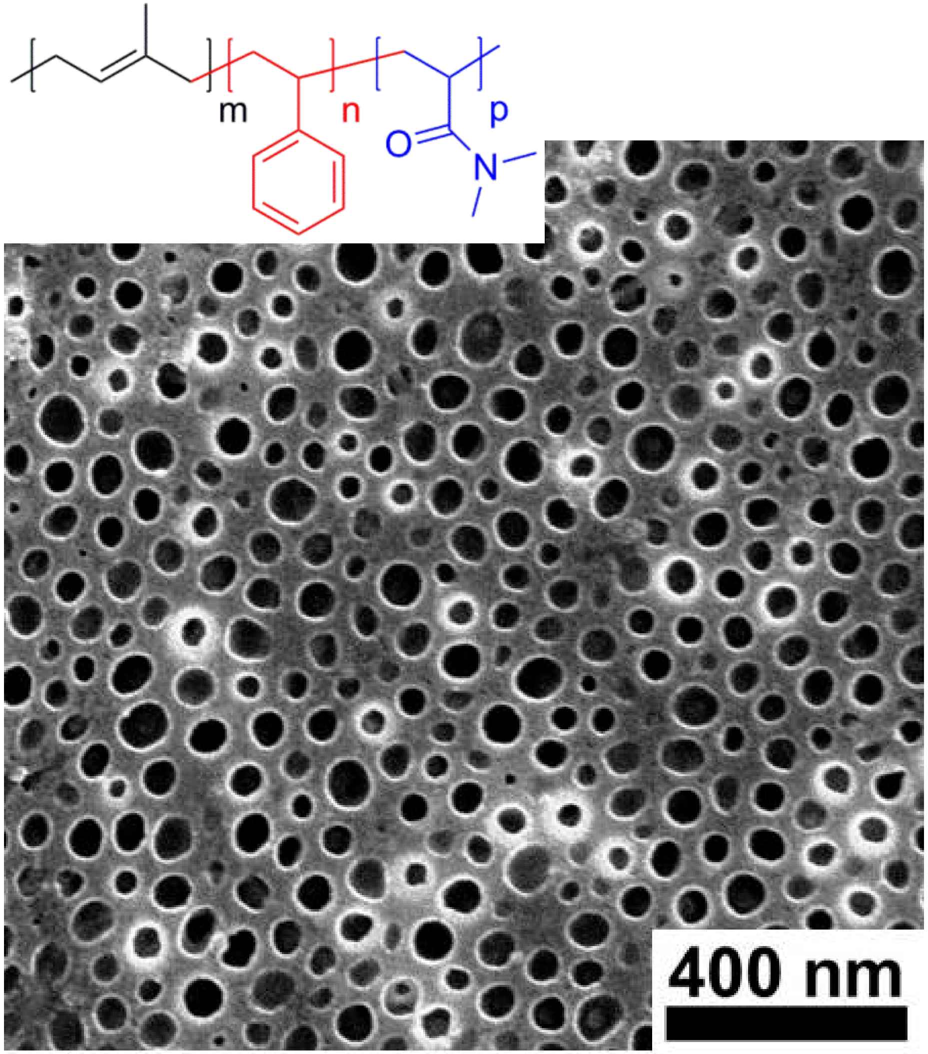
The SNIPS Process is Useful in Multiple Geometries



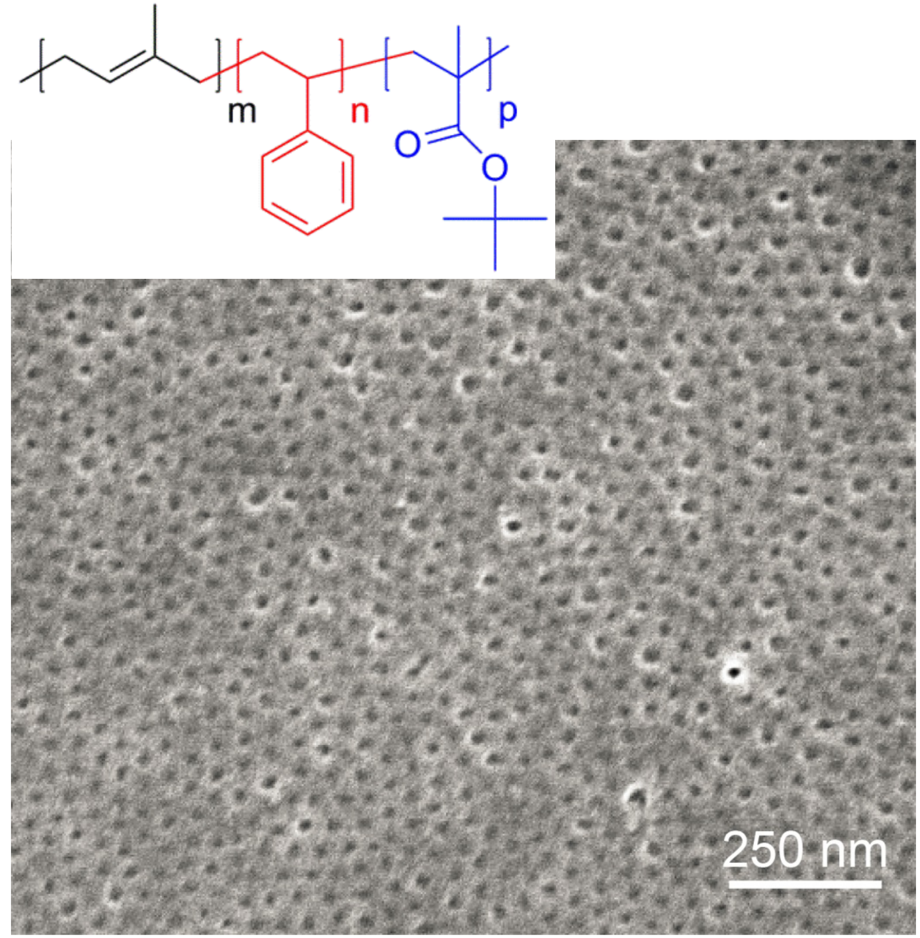
Zhang, Y.; Mulvenna, R. A.; Boudouris, B. W.; Phillip, W. A. *J. Mater. Chem. A* **2017**, *5*, 3358-3370.

Tuning the Chemistry of the Third Block Affects Assembly

PI-PS-PDMA

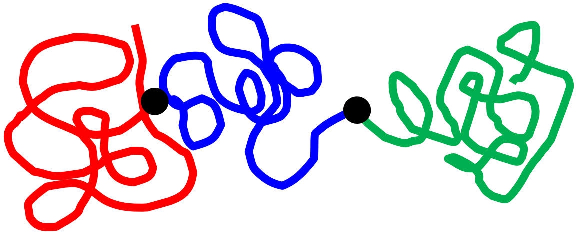


PI-PS-PtBMA



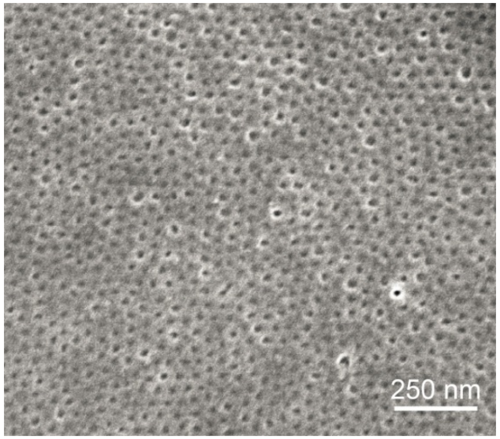
Two-fold Reduction in Dry-State Pore Size Approaches the Desalination Limit

Summary and Future Outlook of Our Functional Polymers



Functional polymers can be synthesized readily using controlled radical polymerization techniques such that chemically-tunable, technologically-relevant macromolecules can be generated in large batches.

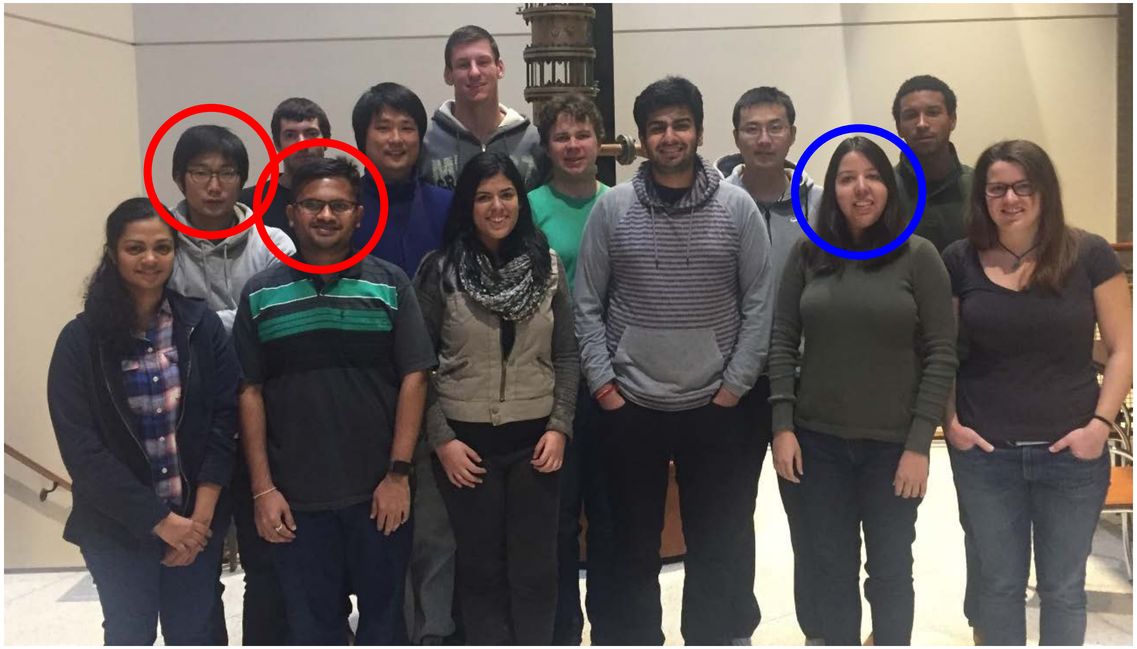
Radical polymers have been synthesized in such a manner that alleviates many of the problems associated with π-conjugated macromolecules. Furthermore, these polymers have been shown to be useful transparent conductors. Finally, open-shell materials were utilized in advanced flexible electronic applications.



Nanoporous flexible thin films have been fabricated from triblock polymer precursors. These films have monodisperse, well-ordered pores that have tunable chemical functionality. As such, they present themselves as useful materials for a multitude of advanced separations. Furthermore, they have demonstrated the smallest separation sizes of any block polymer-based membranes.

Acknowledgements

Boudouris Research Group



- Lizbeth Rostro (Dow); Aditya Baradwaj (Elantas); Sanjoy Mukherjee (University of California, Santa Barbara); Seung Hyun Sung (University of Delaware); Ned Tomlinson (Bostik)
- Ryan Mulvenna (Dow); Darby Hoss (Intel); Jennifer Laster (Intel)

External Collaborators

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- Elaine Zhu (Wayne State)

Purdue Collaborators

- Stephen Beaudoin
- George Chiu
- David Corti
- Elias Franses
- Jianguo Mei
- Jeff Rhoads
- Brett Savoie

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