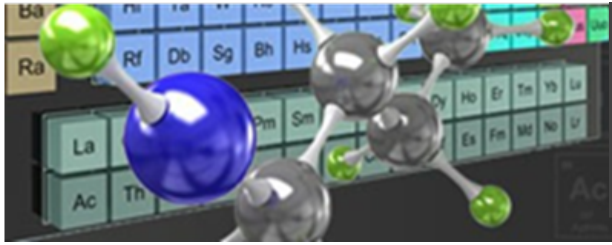

Separation Science and Technology (SST)
as a Convergence Platform for *SusChEM,*
Sustainable Chemistry, Engineering and Materials

Next Generation of Multifunctional Polymeric Membranes for Resource Recovery

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Korea Advanced Institute of Science and Technology (KAIST)

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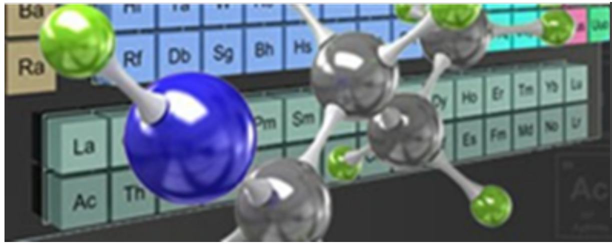
Division of Engineering and Applied Science
California Institute of Technology

San Francisco, August 12-13, 2014

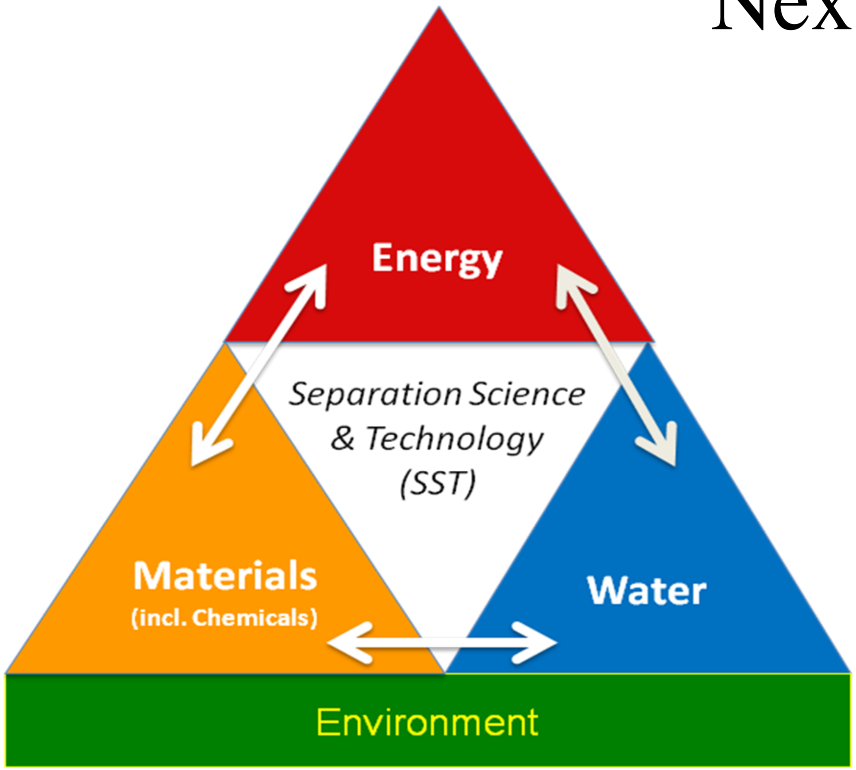
Outline

- **Background**
- **Overview and Summary of Recent Advances**
- **Acknowledgments**



Separation Science and Technology (SST)
as a Convergence Platform for *SusChEM,*
Sustainable Chemistry, Engineering and Materials

Separation Science and Technology (SST) for a Sustainable Energy, Water and Materials Nexus



Separation S&T Platform

Separation Processes
Separation Materials
Separation Systems

Integral Element

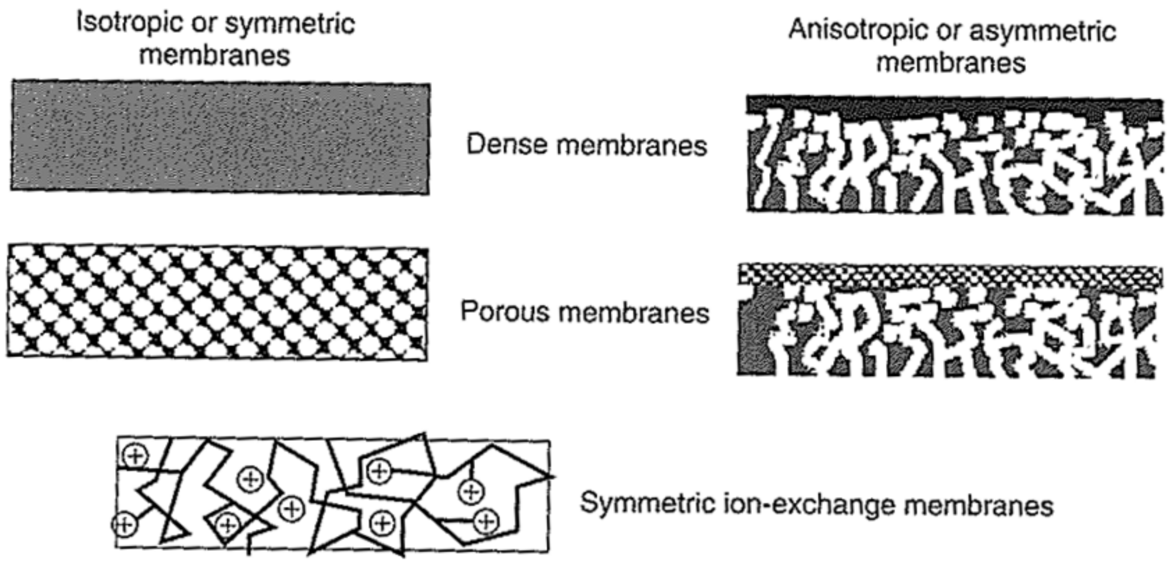
Reclaiming and Maintaining
The Environment

Membrane Technology for a Sustainable Energy, Water and Materials Nexus

- **Polymeric membranes are critical for a broad range of sustainability related applications including**
  - **Energy conversion and storage**
  - **Water treatment, reuse and desalination**
  - **Gas separations**
  - **Biofuel processing**
  - **Metal and resource recovery**
  - **Biochemical separations and purifications**

Current Polymeric Membranes

- **Current commercial polymeric membranes perform a single function such as**
  - **Salt rejection in desalination using a dense and composite membrane**
  - **Particle rejection in algae separations and harvesting using a porous and low-pressure membrane**
  - **Proton transfer in fuel cells by a cation-exchange membrane**



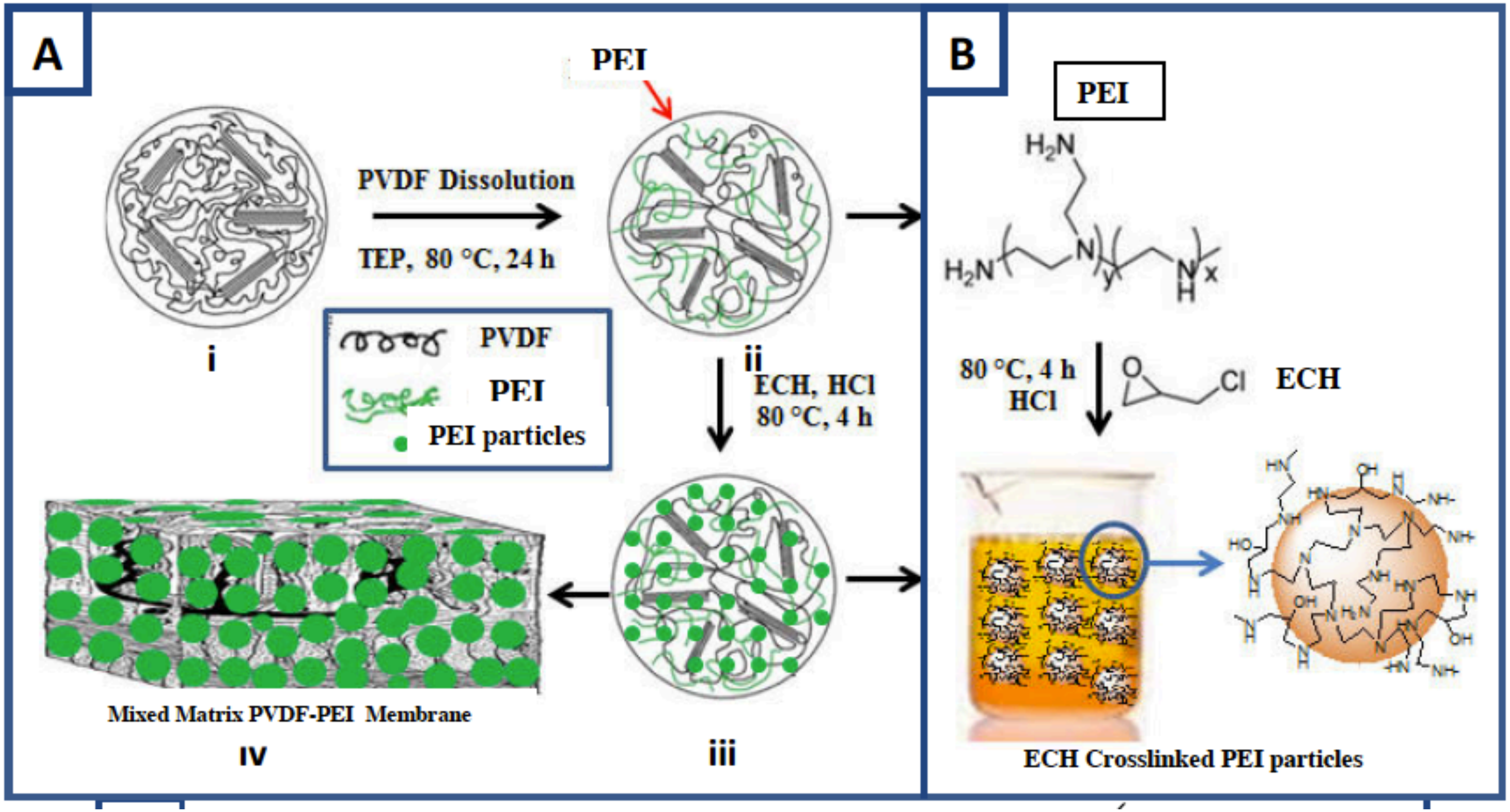
Multifunctional Polymeric Membranes

- **Membrane technology is moving towards advanced membranes that perform multiple functions with improved flux and fouling resistance including:**
  - **Solute rejection**
  - **Sorption**
  - **Catalysis**
  - **Charge transport**

Next Generation Polymeric Membranes: Mixed Matrix Membranes With Emebbeded Nanomaterials

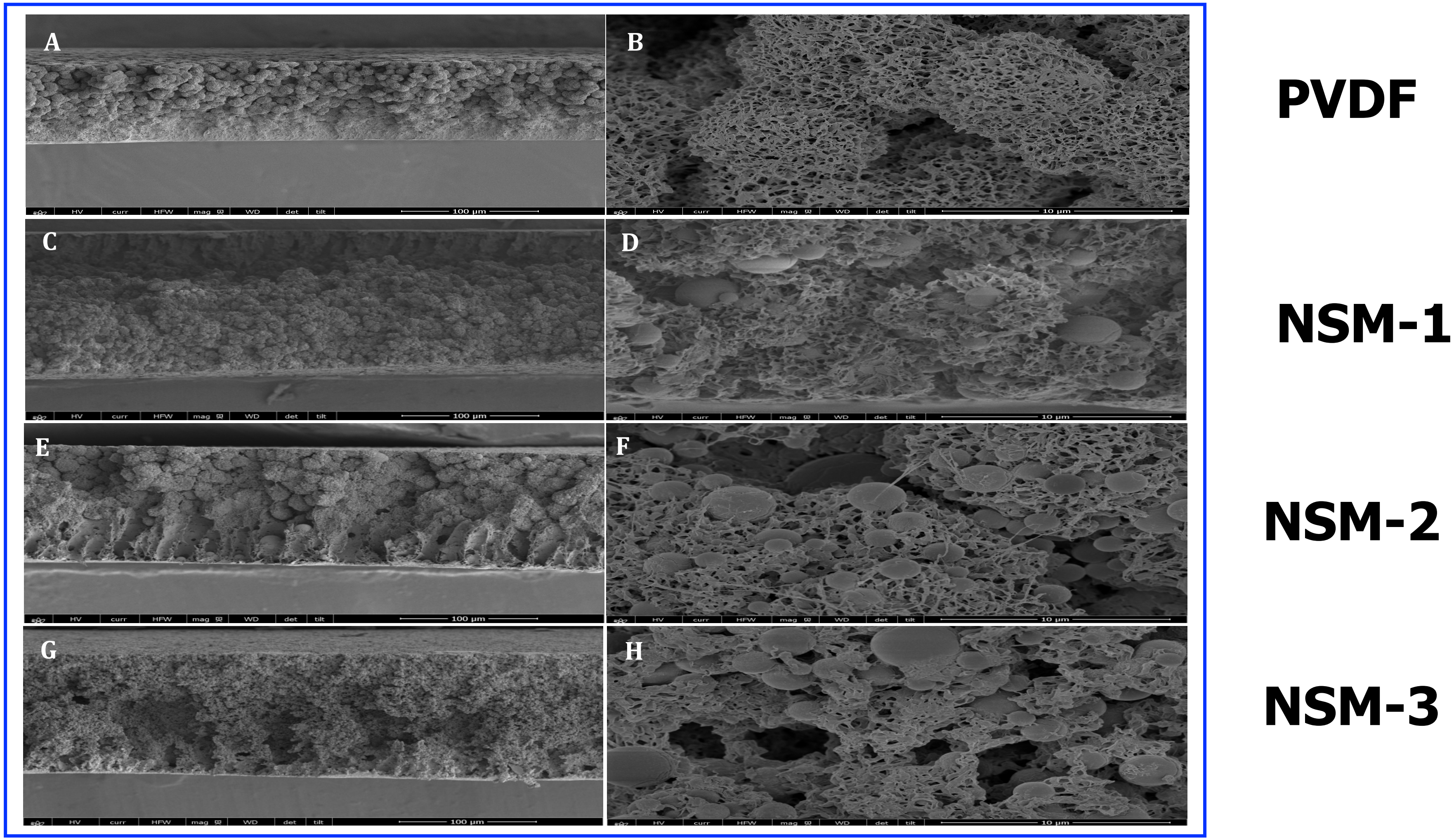
- **Convergence of membrane technology and nanotechnology to prepare mixed matrix and composite membranes with embedded nanomaterials**
  - Carbon nanotubes
  - Graphene
  - Zeolites
  - Metal oxide nanoparticles
  - Metal organic frameworks
  - **Dendritic macromolecules (Our Group)**
  - **Polymeric nanoparticles (Our Group)**

MMMs With In-Situ Generated Polyethyleneimine (PEI) Particles as Weak-Base Membrane Absorbers



Kotte, M. R., Cho, M. and Diallo, M. S. A Facile Route to the Preparation of Mixed Matrix Polyvinylidene Fluoride Membranes with *In-Situ* Generated Polyethyleneimine Particles. *J. Mem. Sci* **.2014**, 450, 93-102.

SEM Images of MMMs With In-Situ Generated PEI Particles



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Composition of MMMs With In-Situ Generated Polyethyleneimine (PEI) Particles

Membrane Composition	NSM-1		NSM-2		NSM-3		PVDF (Neat)	
	Wt , g	Wt, %	Wt, g	Wt, %	Wt, g	Wt, %	Wt, g	Wt, %
PVDF	5.25	**73.32**	5.25	**62.16**	5.25	**52.27**	5.25	**100**
[a] PEI Particles	1.91	**26.68**	3.196	**37.84**	4.794	**47.73**	--	--

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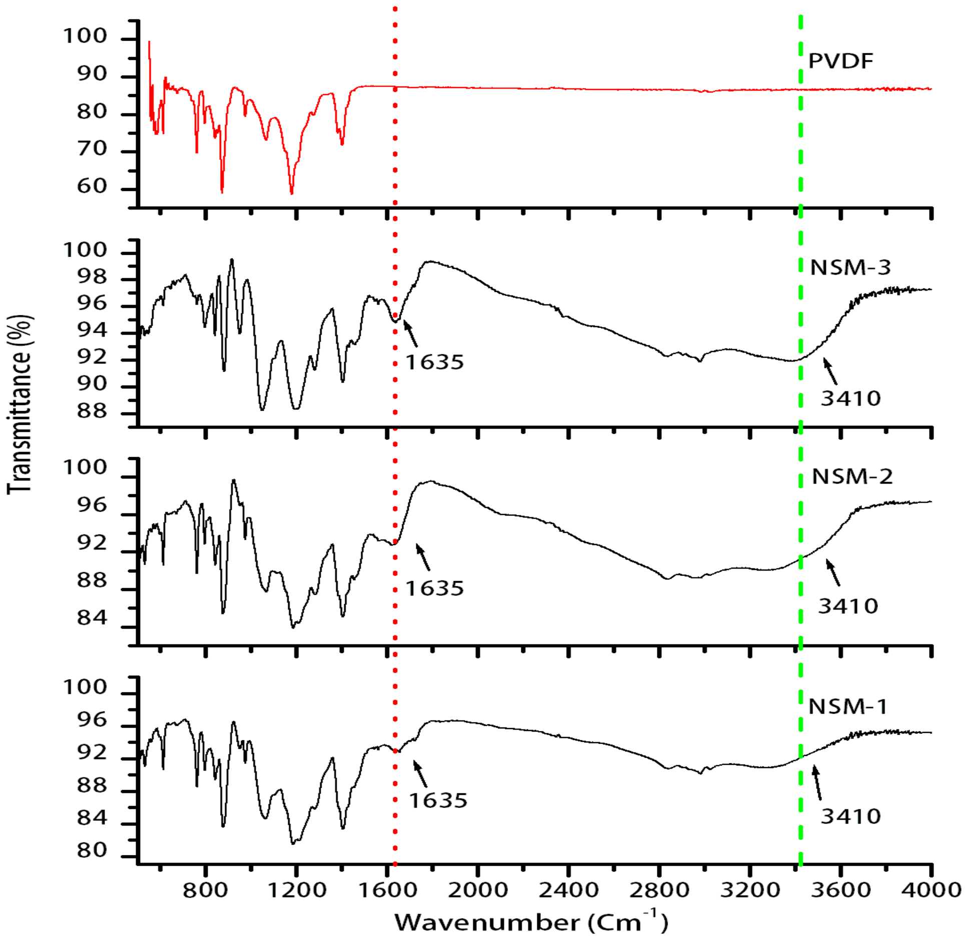
FTIR Spectra of the Control PVDF and With In-Situ Generated PEI Particles



New IR Peaks from PEI particles:

1. **NH_2 bending (1635 cm^{-1})**

2. **NH Stretching (3255 cm^{-1})**

3. **OH stretching (3410 cm^{-1})**

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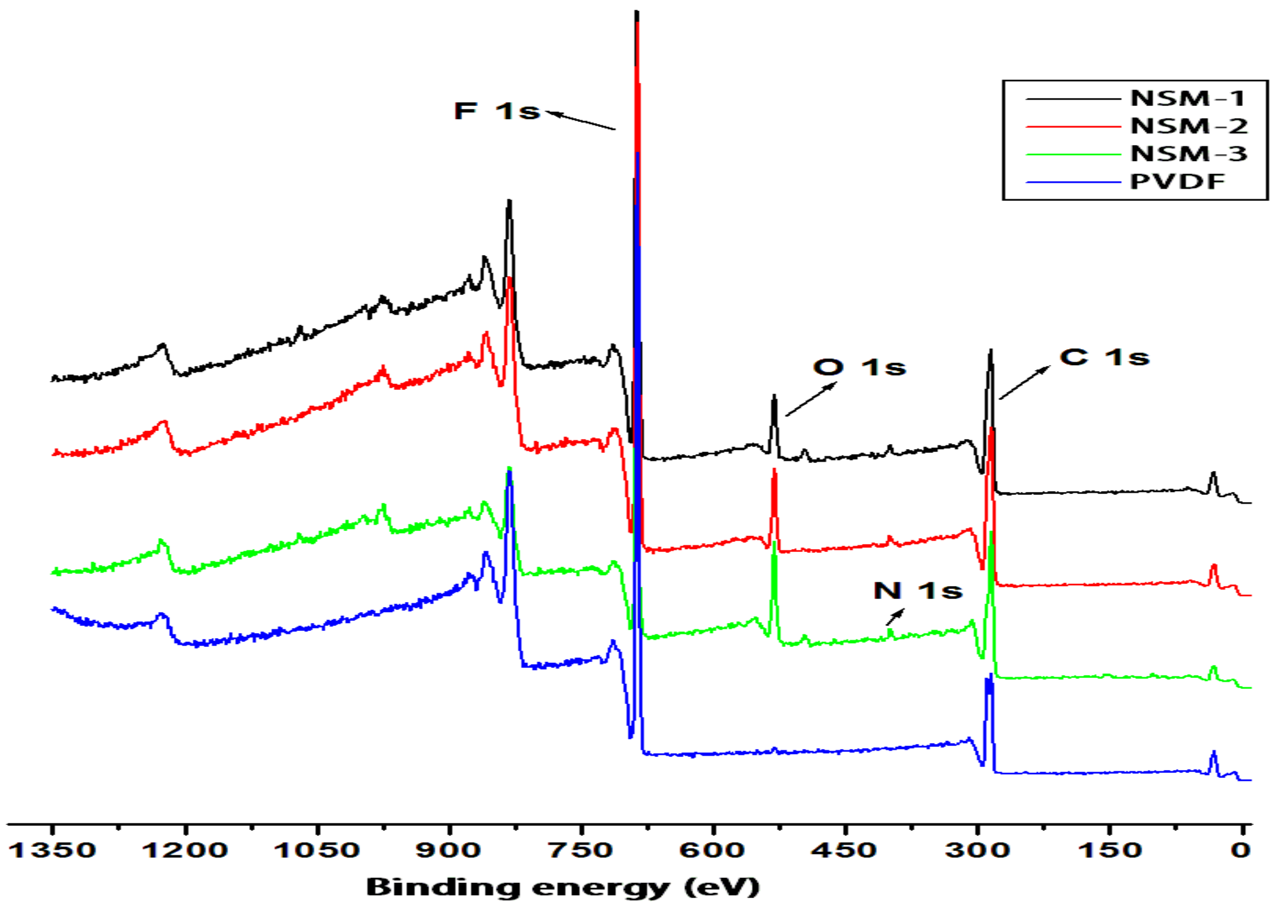
XPS Spectra of the Control PVDF and Mixed Matrix Membranes



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Surface Compositions of MMMs With *In-Situ* Generated PEI Particles As Determined by XPS

Membrane Sample	Concentration (wt%)			
	C	**F**	**O**	**N**
PVDF	51.71	48.29	---	---
NSM-1	53.93	38.2	6.85	1.02
NSM-2	54.46	36.01	8.25	1.28
NSM-3	57.37	28.41	12.38	1.84

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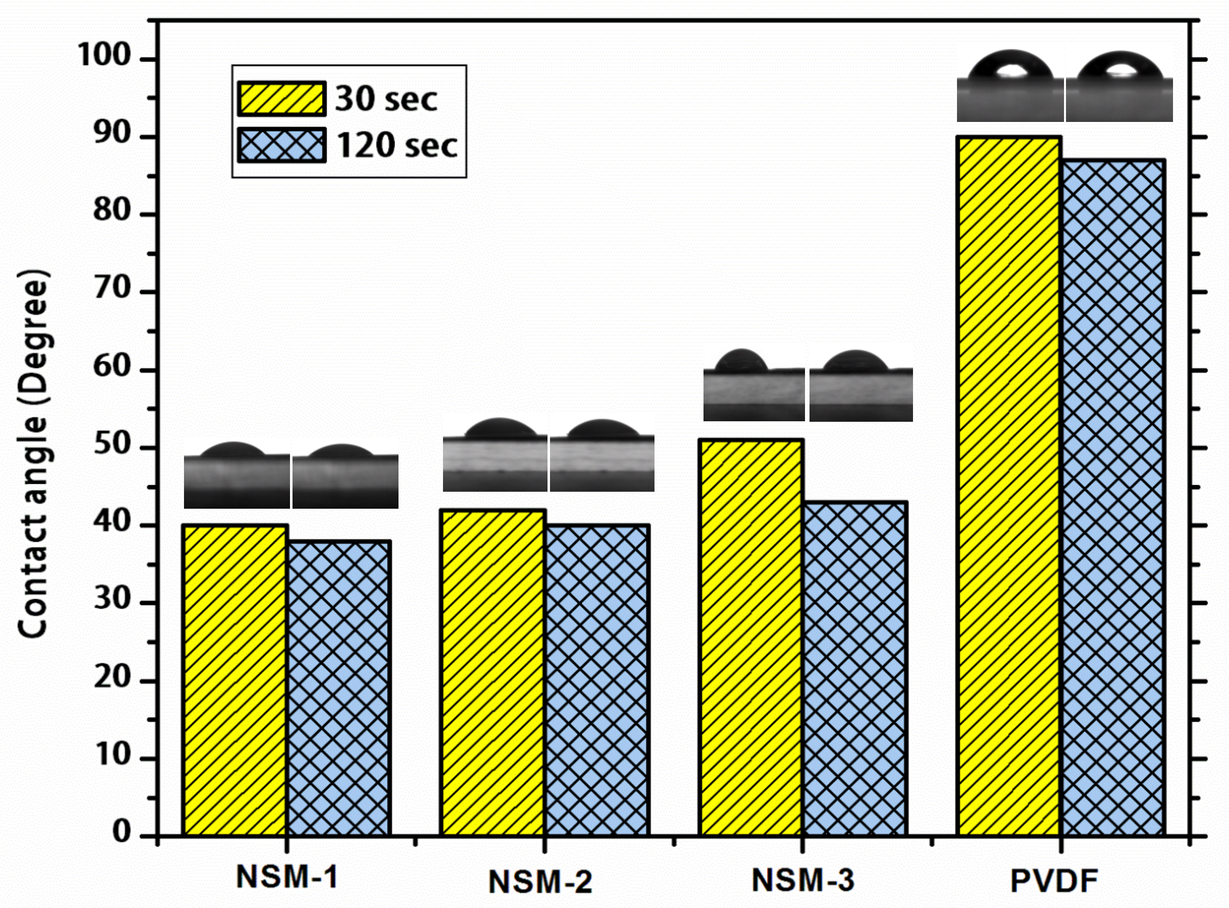
Contact Angles of MMMs With In-Situ Generated PEI Particles



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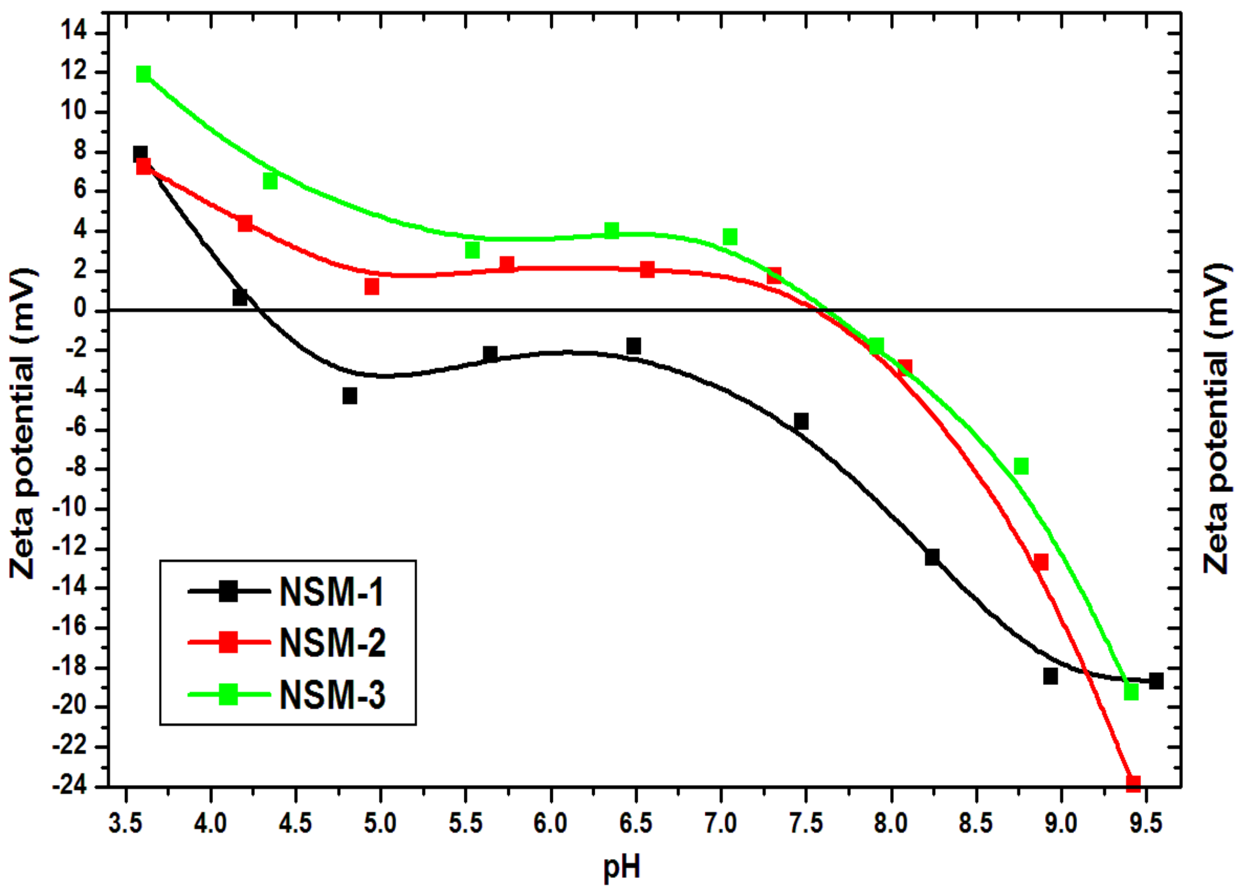
Zeta Potentials of MMMs With In-Situ Generated PEI Particles



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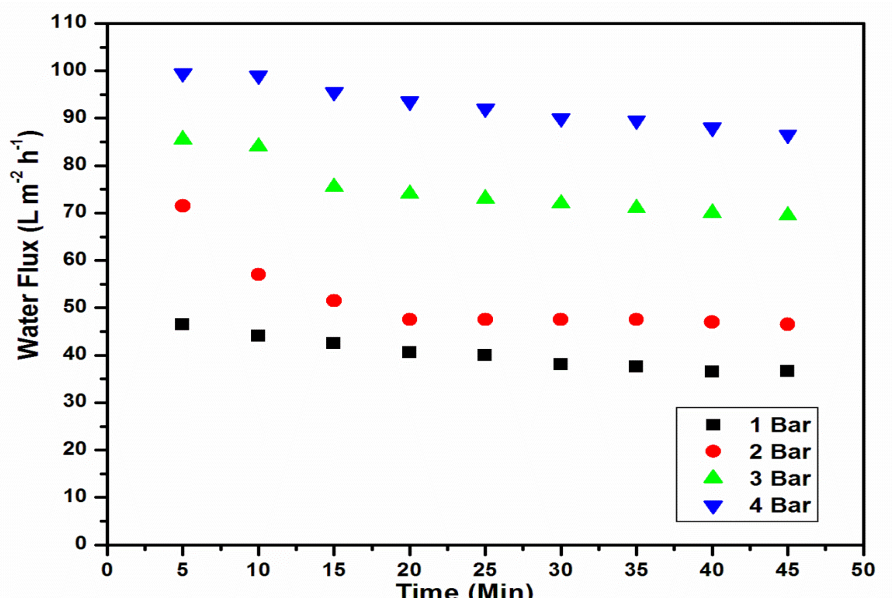
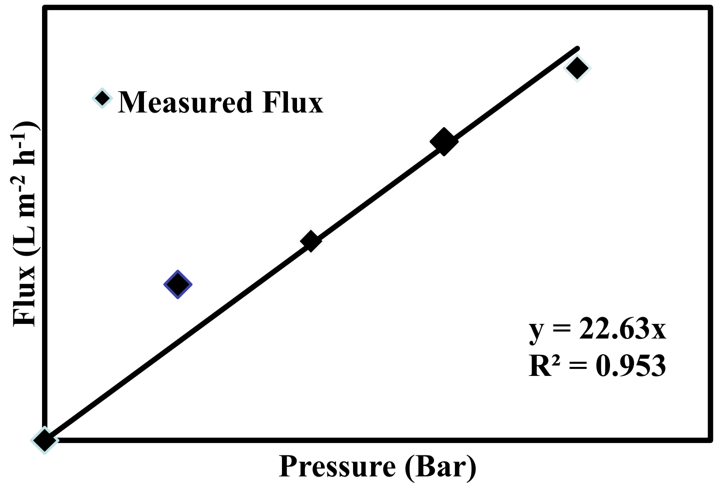
Water Permeability of the NSM-2 Membrane With In-Situ Generated PEI Particles





Water permeability of the NSM-2 membrane is equal to ~23 Liters/m²/hr/bar.

Water permeability of an ultrafiltration (UF) membrane typically varies from 50 to 800 Liters/m²/hr/bar.

NSM-2 membrane behaves as a "tight" UF membrane

Kotte, M. R., Cho, M. and Diallo, M. S. A Facile Route to the Preparation of Mixed Matrix Polyvinylidene Fluoride Membranes with *In-Situ* Generated Polyethyleneimine Particles.*J. Mem. Sci* **.2014**, 450, 93-102.

Protein Binding Experiments: Protocol

The NSM-2 membrane was employed in these experiments

Run 1: Pure water (Compaction) Feed: DI water; pH: 6.0 Pressure: 1 Bar Compaction: 30 min	**Run 2: Pure water flux (run)** Feed: DI water; pH: 6.0 Pressure: 1 Bar Run time: 60 min
Run 3: BSA solution (run) Concentration: 1000 mg/L pH: 6.50 Run time: 60 min Pressure: 1 Bar	**Run 4: DI water wash (cleaning)** Membrane cleaning in DI water under stirring Cleaning time: 60 min
Run 5: Pure water flux (post cleaning run) Feed: DI water pH: 6.0 Pressure: 1 Bar Run time: 60 min	

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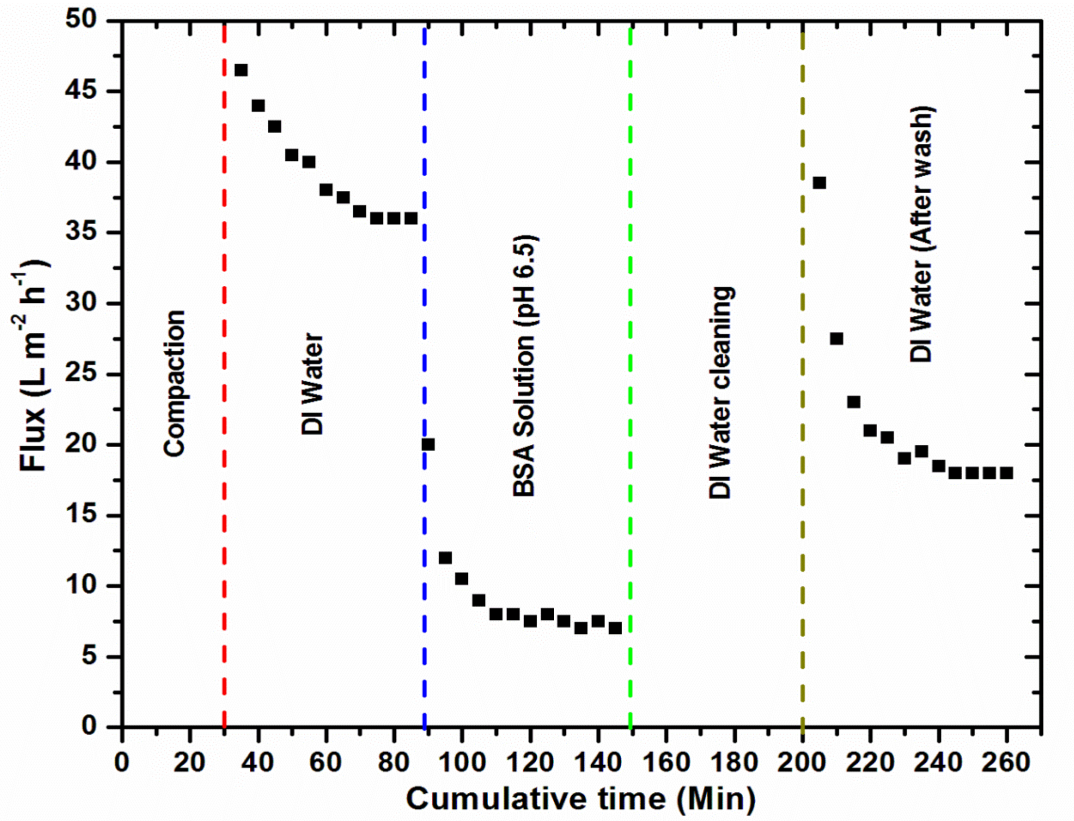
Protein Binding Experiments: Results

The NSM-2 membrane was employed in these experiments



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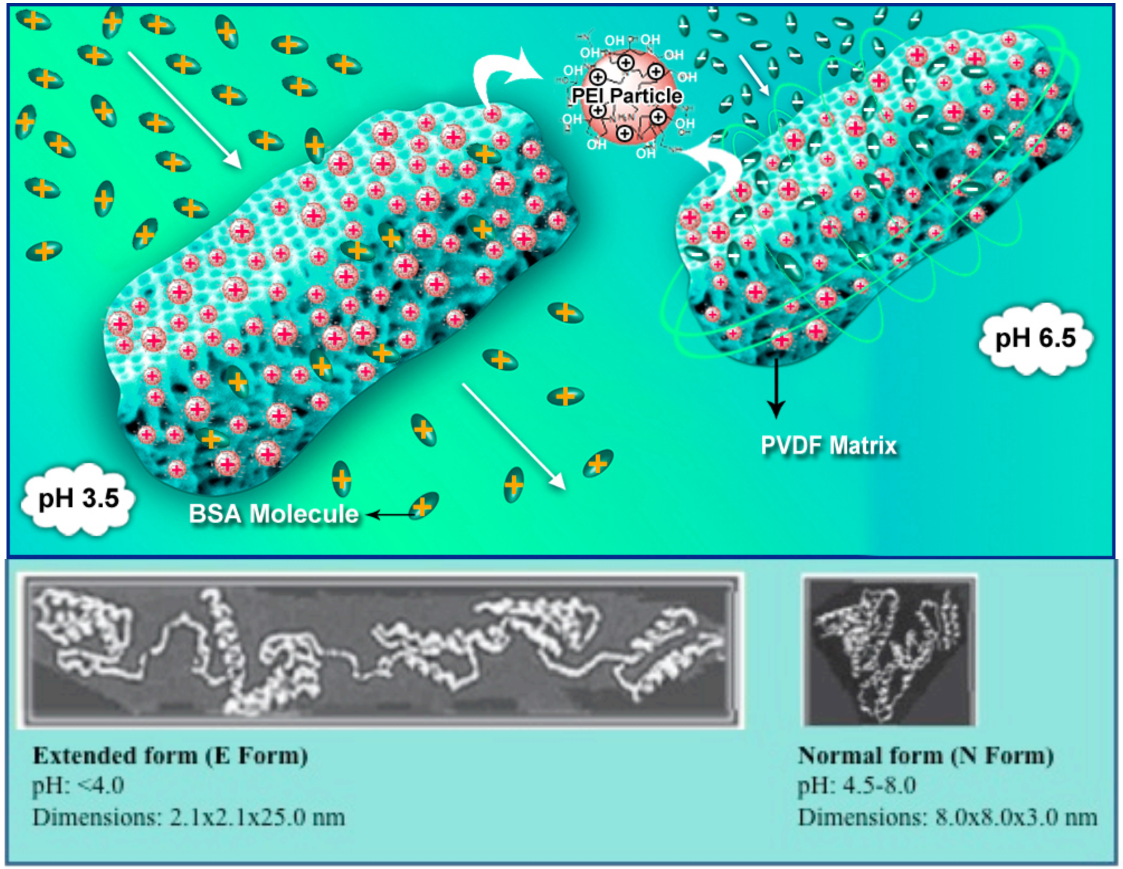
MMMs With In-Situ Generated PEI Particles as Weak-Base Membrane Absorbers

BSA: Bovine Serum Albumin Protein (1000 mg/L)



NSM-2 UF Membrane

Pressure = 1 bar

Particle loading: 38 wt%

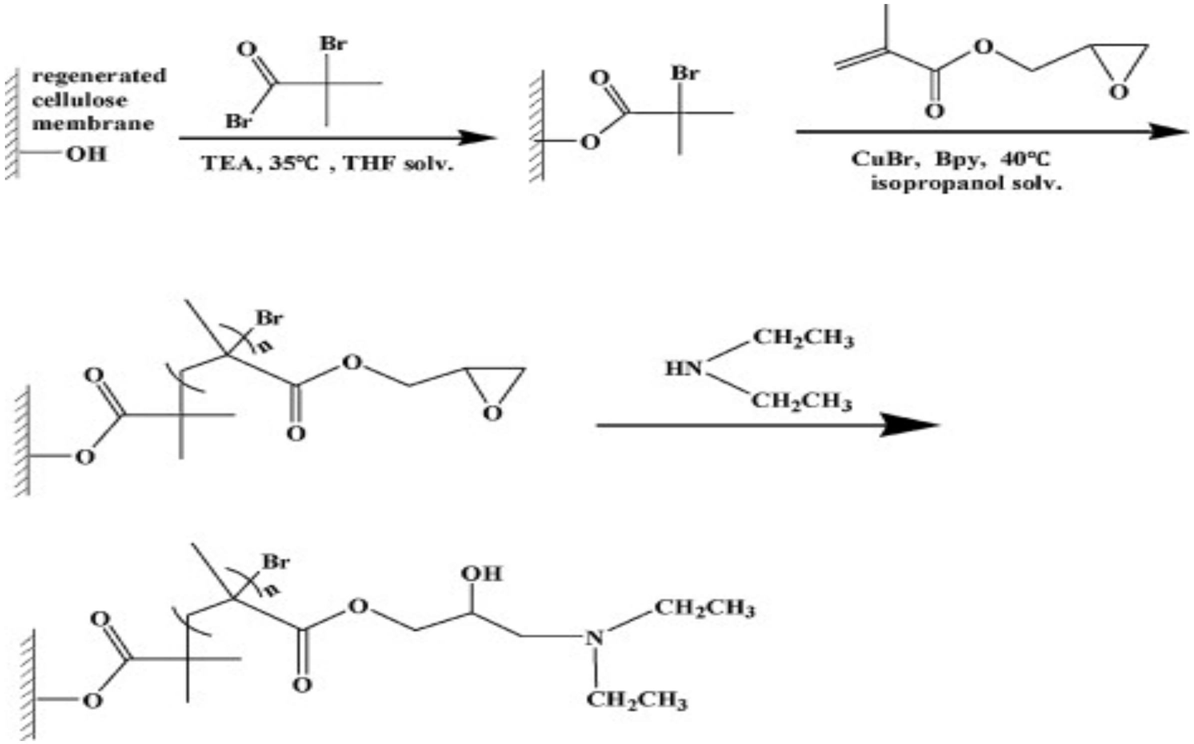
BSA rejection: 90%

BSA binding capacity; 105 mg of protein per mL of membrane at pH 6.5

Kotte, M. R., Cho, M. and Diallo, M. S. A Facile Route to the Preparation of Mixed Matrix Polyvinylidene Fluoride Membranes with In-Situ Generated Polyethyleneimine Particles. J. Mem. Sci ***.2014****, 450, 93-102.*

Other Reported Preparation Routes for Weak-Base Membrane Absorbers

Surface-initiated atom transfer radical polymerization

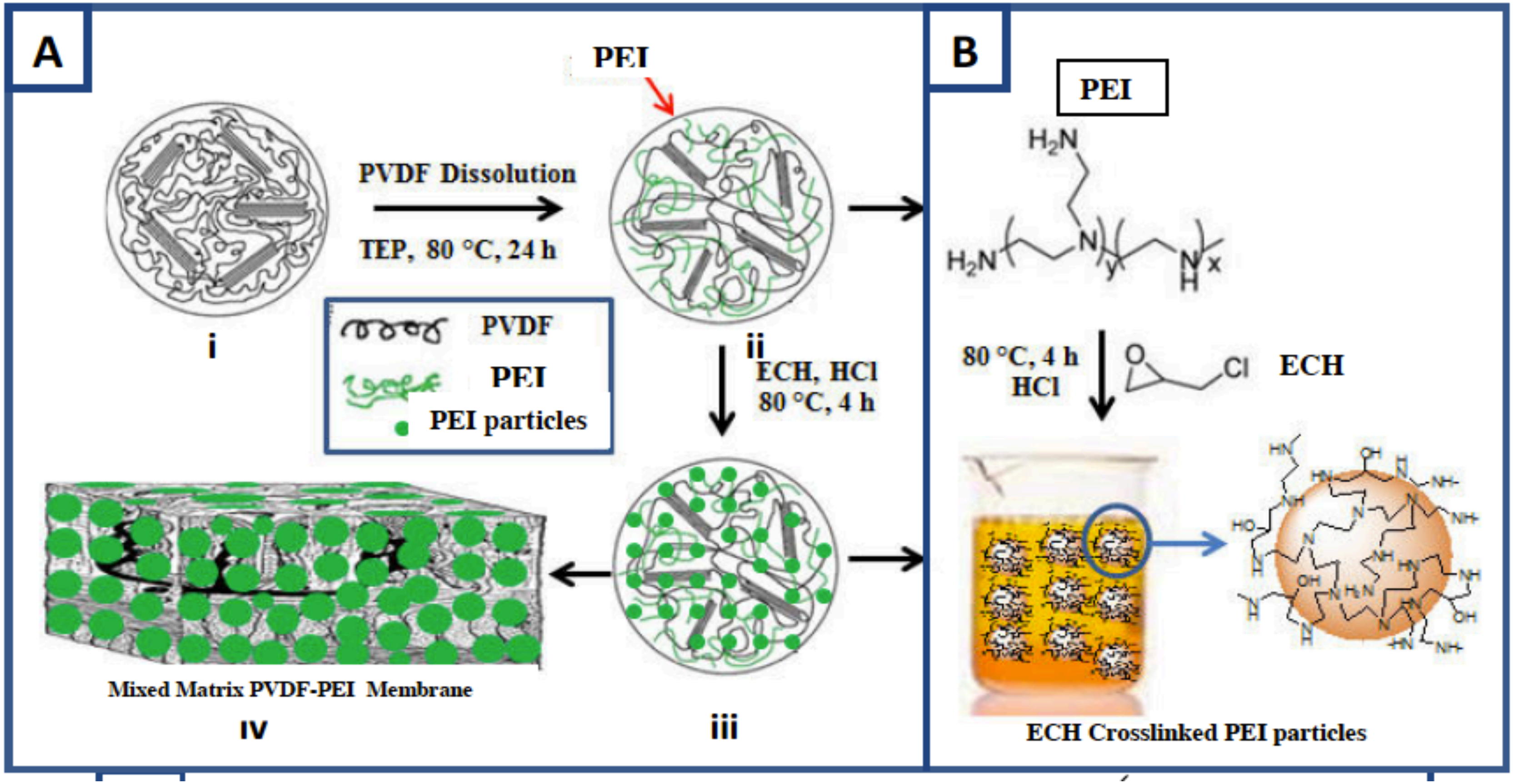


BSA binding capacity: 96 mg of protein per mL of membrane in PBS buffer (pH ~7)

Qian et al. *Appl. Surf. Sci*. 271, **2013**, 176–183

Our Approach for Preparing Weak-Base Membrane Absorbers: One Pot Synthesis

No surface-initiated atom transfer radical polymerization is needed



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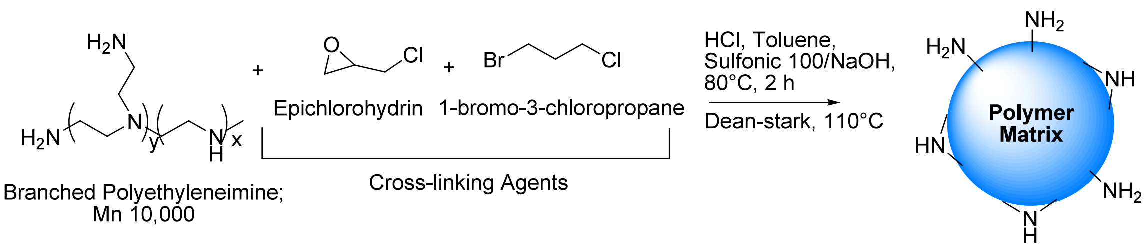
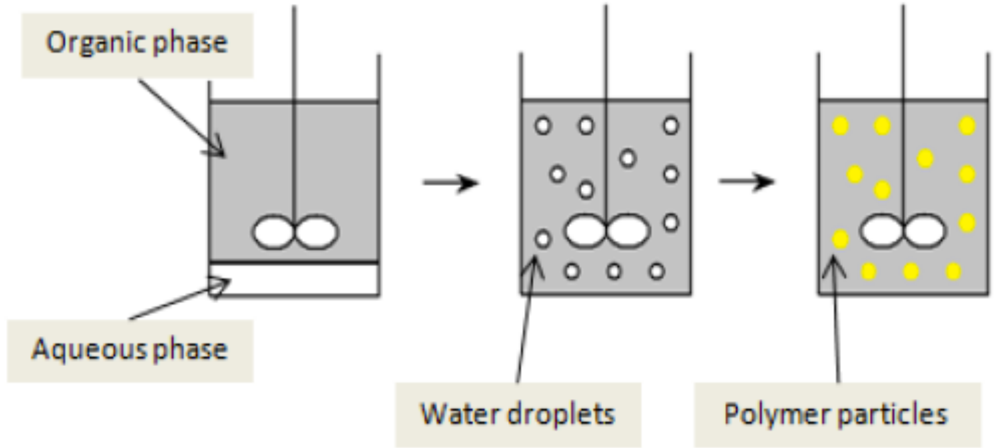
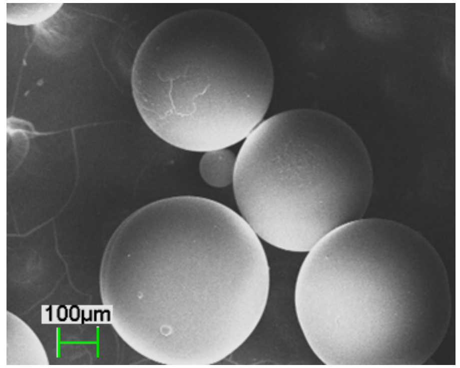
Our Approach for Preparing Weak-Base Membrane Absorbers: In-Situ Synthesis of PEI Particles in the Casting Solutions

No prior synthesis of the PEI particles by inversion suspension polymerization is needed

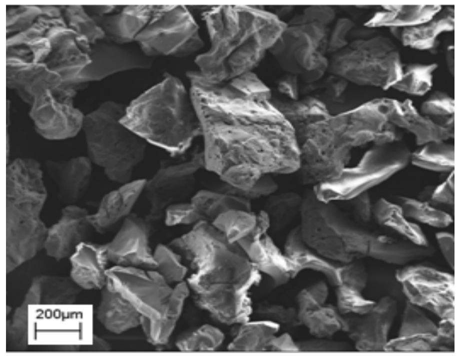




Suspension crosslinking



Bulk crosslinking ♪



Diallo, MS and co-workers Branched polymeric media: perchlorate-selective resins from hyperbranched polyethyleneimine. *Environ. Sci. Technol*. **2012**. 46:10718-10726.

Acknowledgments

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