Preparing Nanostructured Membranes from Benign and Naturally-occurring Reagents

Idris Yazgan, N. Du, R. Congdon, V. Okello and O. Sadik

Department of Chemistry

State University of New York-Binghamton

Center for Advanced Sensors & Environmental Systems

SUN-SNO-GN International Conference, Laguna Palace, Venice, Italy March 9-11, 2015

BINGHAMTON UNIVERSITY
STATE UNIVERSITY OF NEW YORK

Objectives

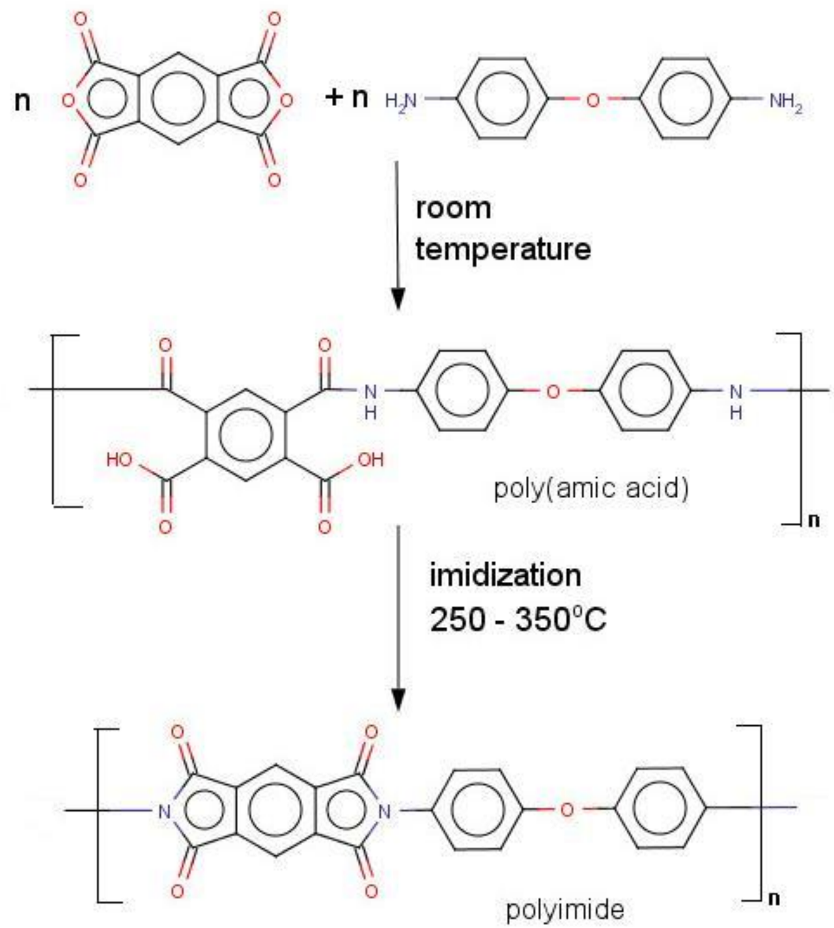
- Incorporate biological building blocks into synthetic, nanostructured PAA membranes
- Develop nanostructured green polymer membranes, with controllable pores for water disinfection that can be used in;
  - Home based drinking systems
  - Remote areas
    - Especially during natural disaster

Research Needs

- Water treatment has been accepted as one of the most crucial topics for a sustainable environment
- US EPA’s Safe Drinking Water Act (SDWA) requires that all surface water be filtered and disinfected before consumption
- Need to develop low-cost, innovative technologies that can efficiently remove microbial contaminants from drinking water.

Poly(amic) acid (PAA)

- PAA
  - Precursor of Polyimide (PI)
  - Powder or liquid, poor mechanical properties
- PI
  - Final product
  - Thin film, flexible, durable



PMDA - pyromellitic dianhydride

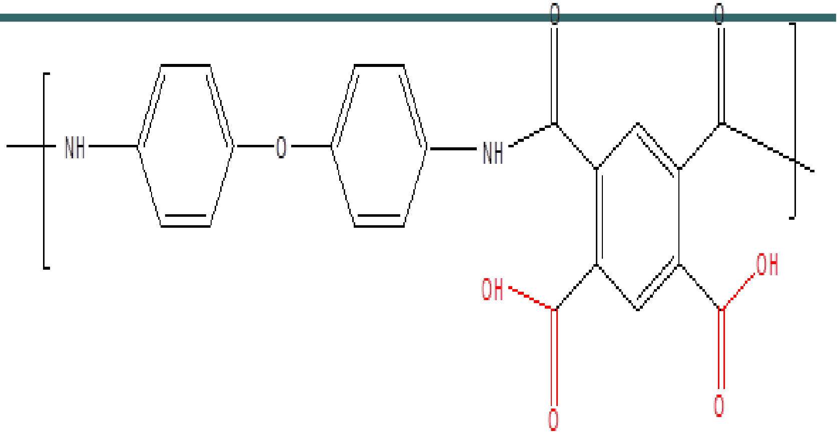
ODA - 4, 4’-oxydianiline

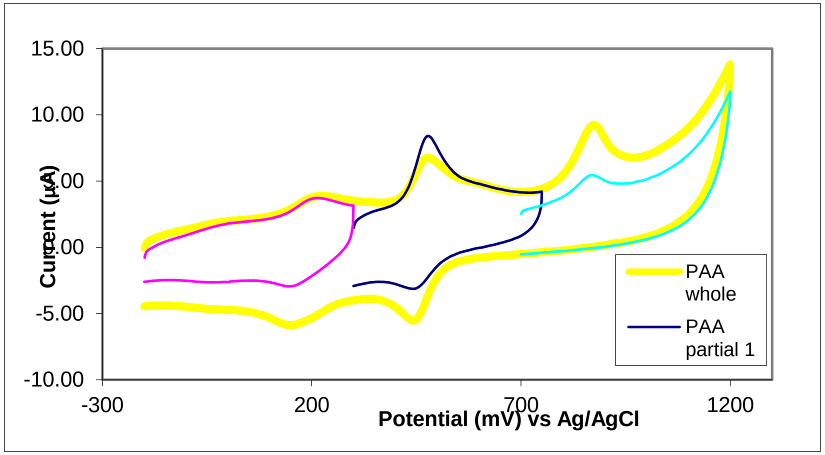
DMAc - N,N-dimethylacetimide

BINGHAMTON UNIVERSITY
STATE UNIVERSITY OF NEW YORK

What is PAA?

- Conductive
- Ease of preparation
- Flow of electronic charges
- Redox stable
- Surface functional groups
- Permeability





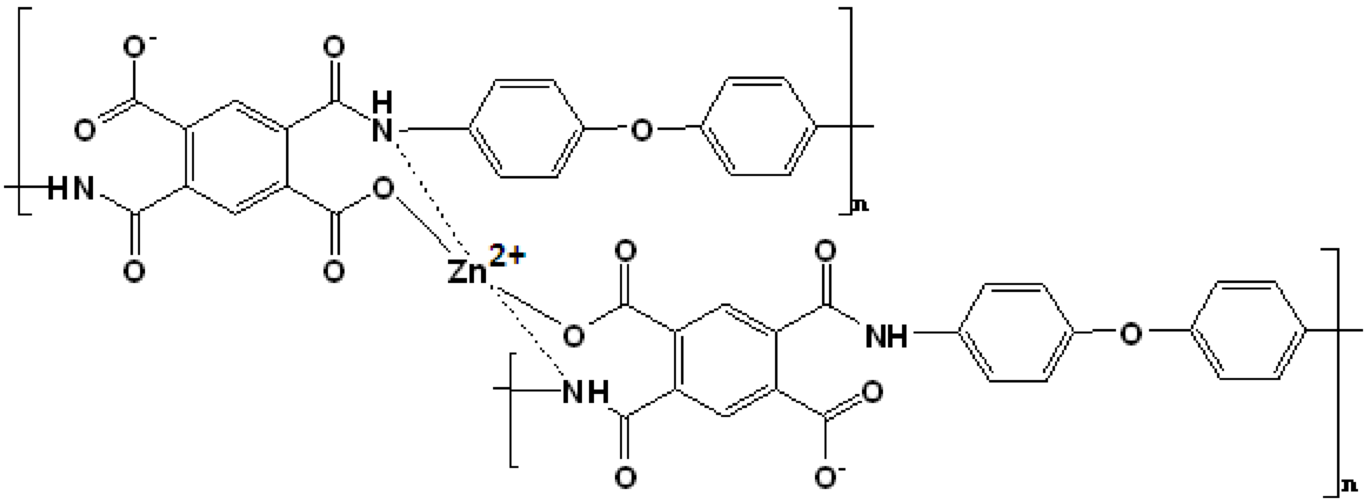
Why PAA Membranes?

- Easy to incorporate bio-functional groups
  - Non-soluble membranes
- Controllable nano-pore size
- Potential for biodegradation
- Conductive and electroactive
- Membranes are simple to manufacture
- Membrane are often disposable; eliminating the need for lengthy cleaning and regeneration
- Reduced footprint

Sadi et al, Langmuir **2010**, 26 (17), 14194–14202

BINGHAMTON UNIVERSITY
STATE UNIVERSITY OF NEW YORK

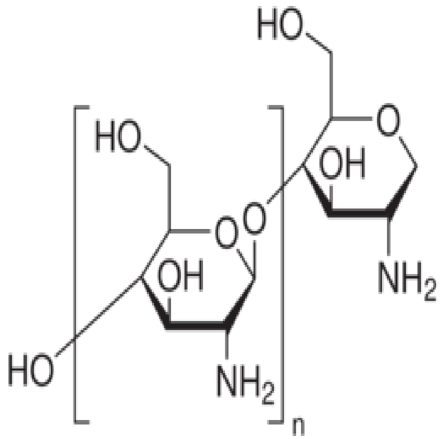
Improving Mechanical Strength



Addition of metal cation may improve mechanical properties by creating complexation networks:

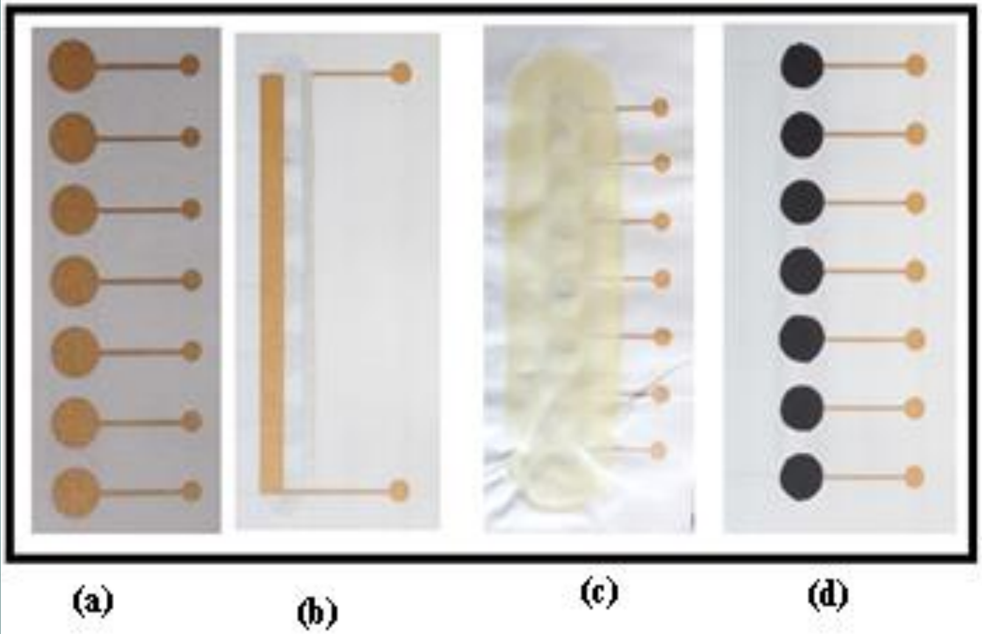
Biological Building Blocks

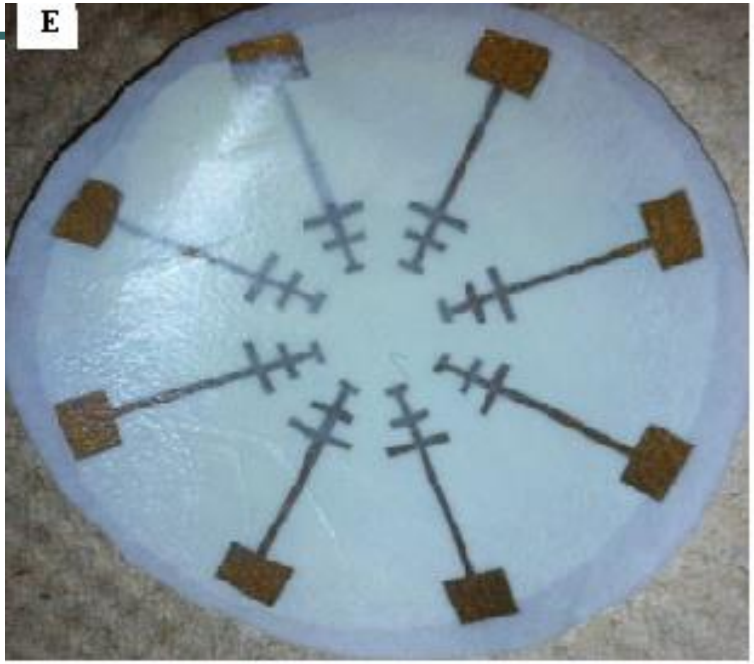
- Chitosan:
  - *Natural and soluble polymer*
  - *Can be used in many formats as membrane*
  - *Can be chemically modified*
  - *Possesses anti-microbial property*
  - *Pre-filtration membrane*



Polymer 50 (2009) 3661–3669
Separation and Purification Technology 75 (2010) 358–365

Previous Applications: Paper-based PAA sensors

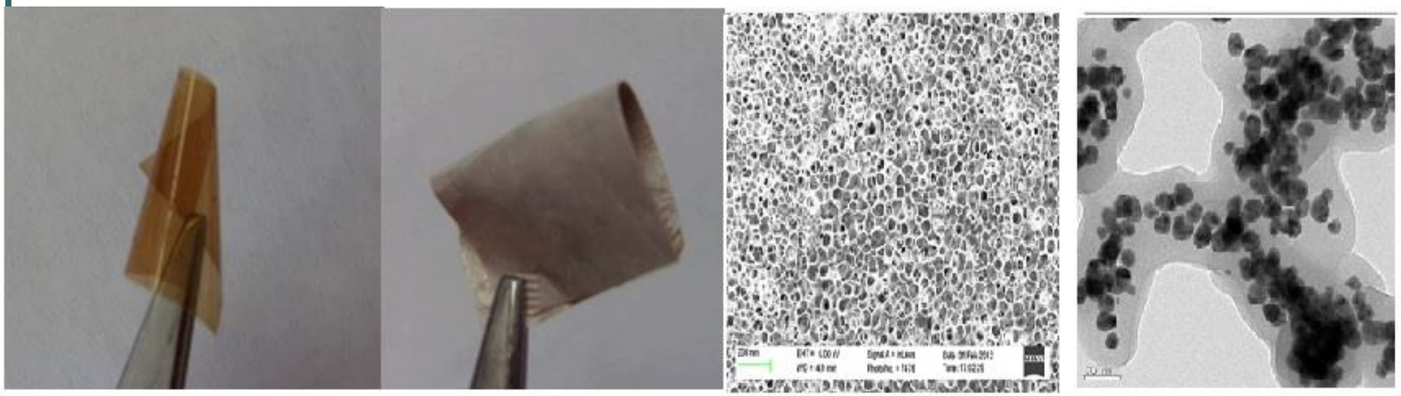




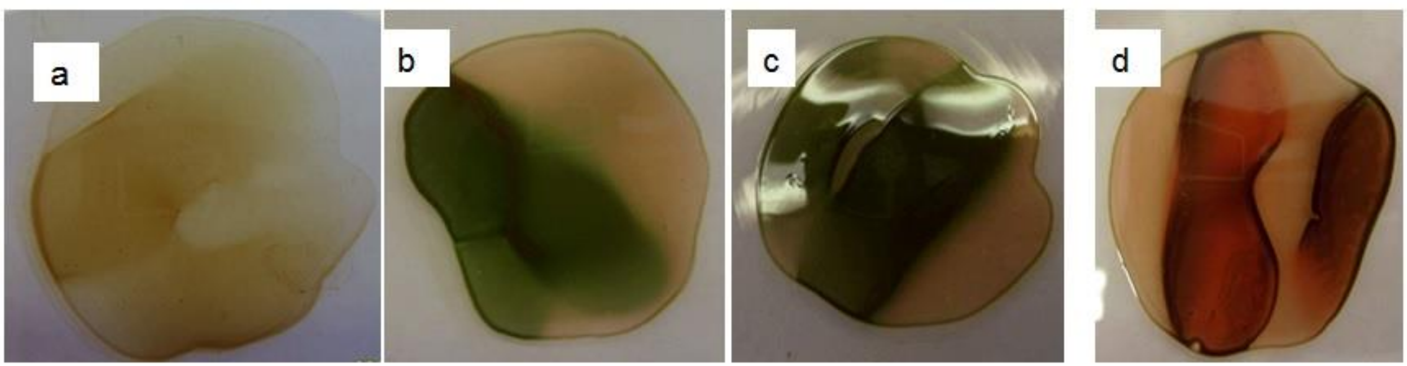
Sample PAA-on membrane electrodes (a) gold working electrodes on paper substrates, (b) gold counter and silver/silver chloride electrodes, (c) Working electrodes coated with PAA membranes, and (d) carbon working electrodes. Right: Gold array electrodes fabricated onto paper substrates; with subsequent coating of PAA membranes (notice the shiny PAA).

Yazgan I., Sadik O., Bushlayer V., et. al, Journal of Membrane Science 2014(in press)

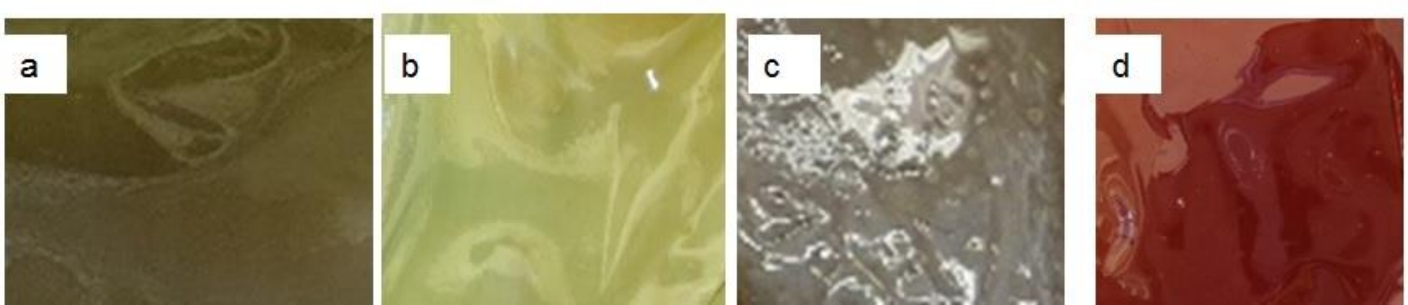
Classic PAAs



- Stable :300℃
- Flexible
- Mechanically strong
- Porous

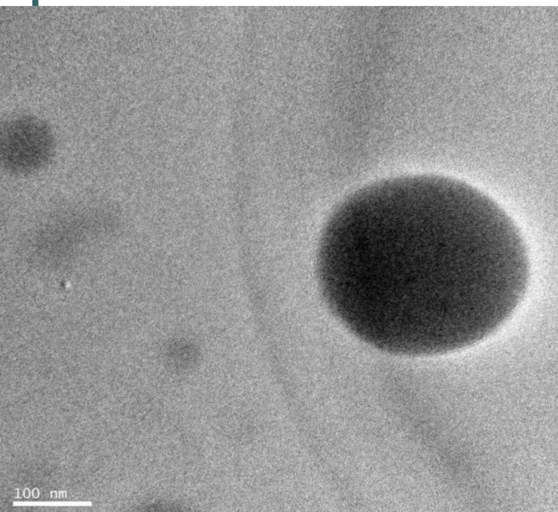


Temperature dependence of PAA a-75 ° C,b-150° C,c-250° C,d-300° C

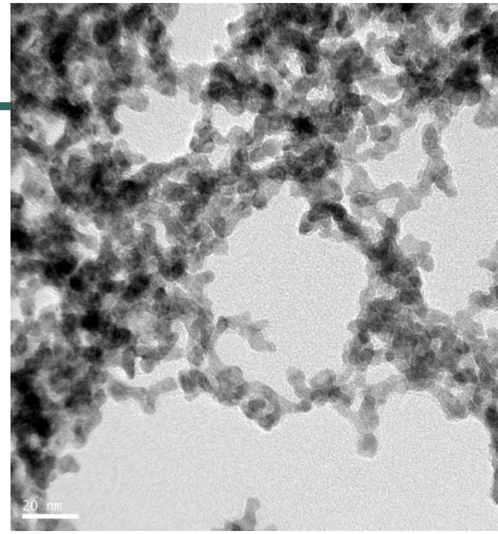


Fluorescent PAA biomembranes: A-PAA-CS with %0.3 GA, B-PAA-DA, C- l-PAA 15 h incubation D- m-PAA-DA with for 15 h

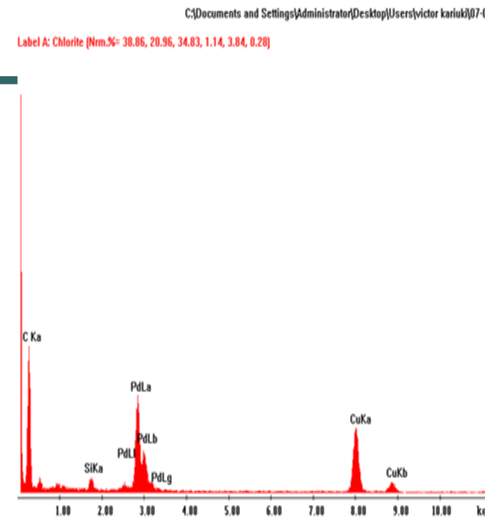
PAA stabilized nanoparticles while maintaining wettability

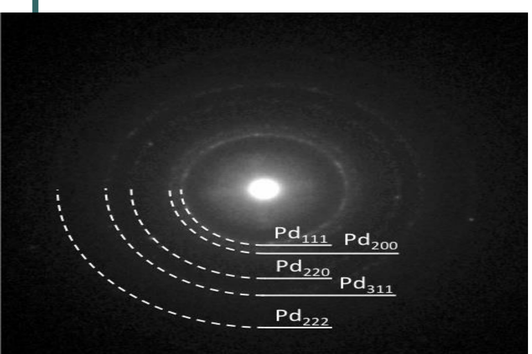


PdNPs stabilized with PAA

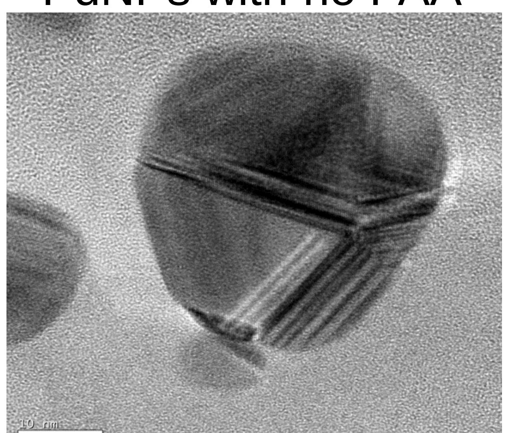


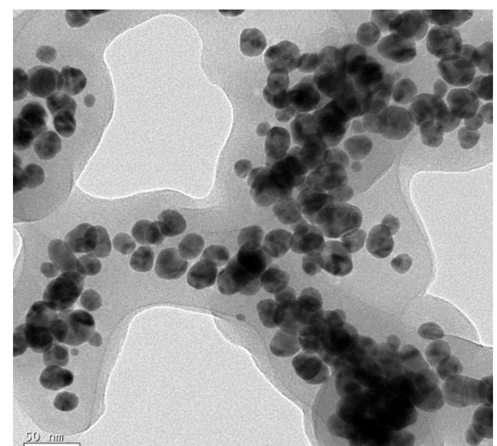
PdNPs with no PAA





X-ray diffraction pattern shows crystalline particles were formed with uniform size & random size distribution.





HRTEM of nanosilver with PAA: Particles are twinned with 5 fold symmetry

Synthesis of PAA and PAA-CS membrane

A

ODA+PMDA in DMAC
(+CS)

↓ rt. 20 h at 200 rpm
under dark

Viscous PAA solution

↓

Phase-inverted membrane synthesis
in 2.5 mg/mL glutaraldehyde solution

↓ 30 minute
incubation

1h incubation
in pure water

↓

Dry at r.t
store under dark

B

ODA+PMDA in DMAC
(+CS)

↓ rt. 20 h at 200 rpm
under dark

Viscous PAA solution

↓

Phase-inverted membrane
synthesis in pure water

↓

1h incubation
in pure water

↓

Dry at r.t
store under dark

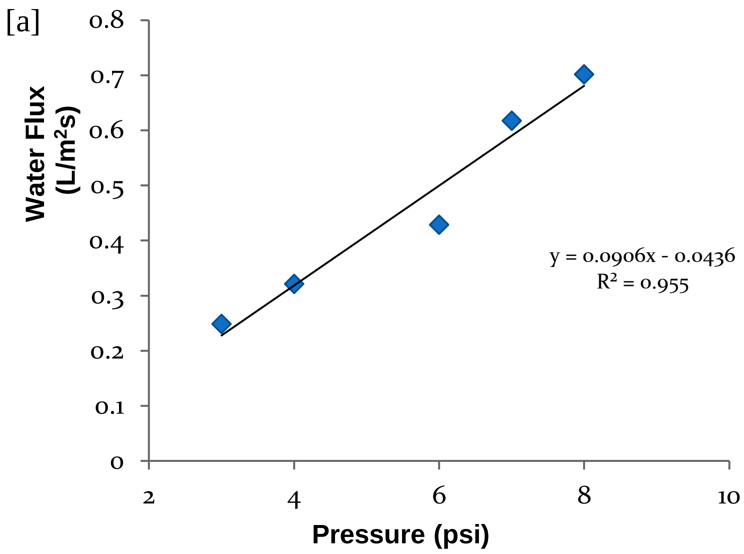
Pore-size Characterization

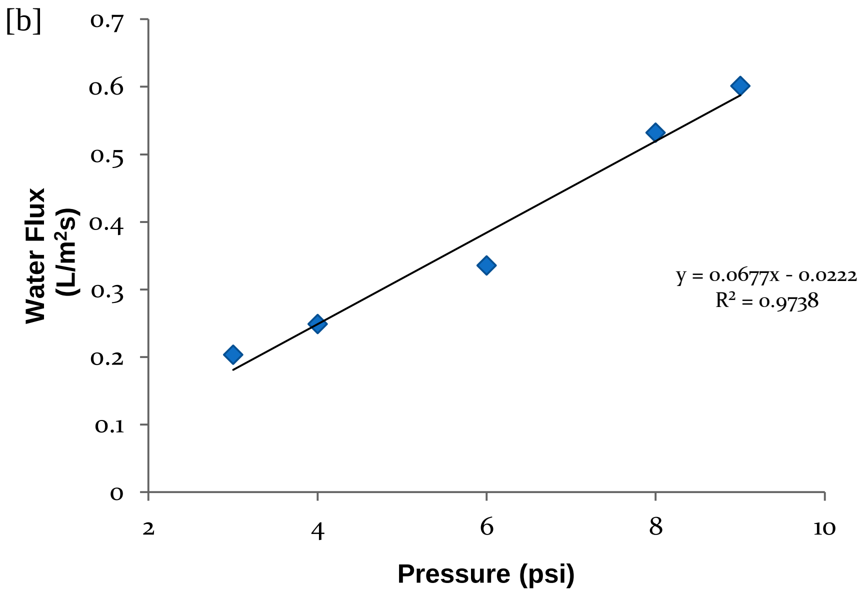
Membranes	Pore size range (nm)	Medium pore size (nm)	Standard deviation (nm)
0.2M PAA	23-158	82	38
0.2M PAA-GA	12-143	67	23
0.25M PAA	11-100	36	25
0.25M PAA-GA	12-104	34	28
0.25M PAA-CS	10-86	41	23
0.25M PAA-CS-GA	9-76	33	25
0.3M PAA	8-84	28	19
0.3M PAA-GA	5-76	18	11
0.3M PAA-CS	6-42	15	12
0.3M PAA-CS-GA	4-45	14	9
0.32M PAA	6-79	27	14
0.32M PAA-GA	4-47	24	9.8
0.32M PAA-CS	5-35	18	8.3
0.32M PAA-CS-GA	4-32	14	6.7

Mechanical Characterization

Membrane	Maximum load (lb)	Tensile strength (ksi)	Modulus of elasticity (ksi)
PAA[a]	6.1	1.5	48.9
PAA-CS[a]	2.8	0.7	43.5
PAA-GA[b]	7	1.8	82.4
PAA-CS-GA[b]	8.6	2.1	71.8
PAA-GA[c]	1.7	0.4	46.1
PAA-CS-GA[c]	3.6	0.9	52.6
PAA-CS-GA in GA[d]	1.3	0.3	35.6

Water Flux-Pressure Pattern





(a) Water flux-pressure pattern of PAA-GA; (b) Water flux-pressure pattern of PAA-CS-GA

BINGHAMTON UNIVERSITY
STATE UNIVERSITY OF NEW YORK

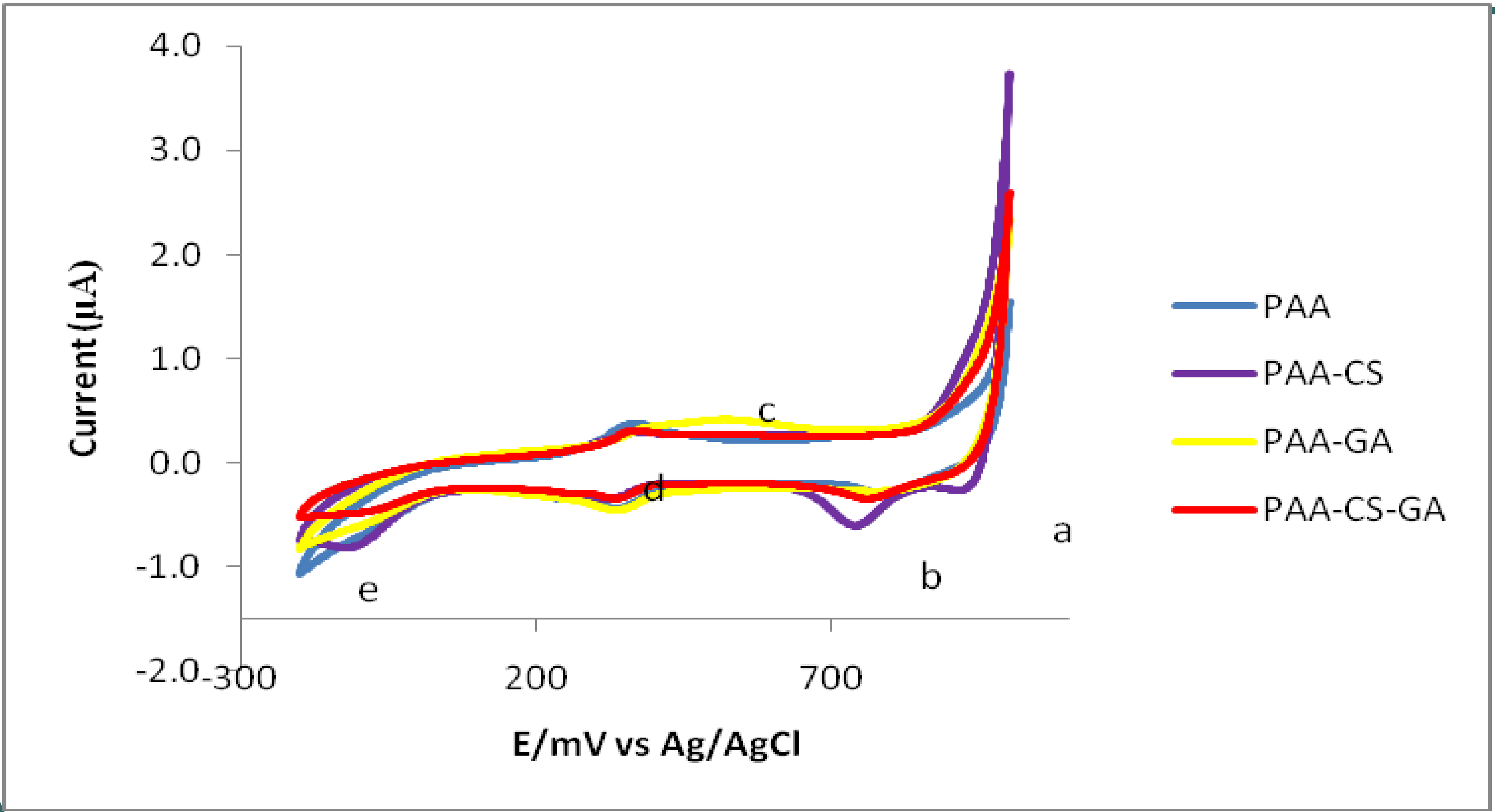
Contact Angle of PAA membranes

Membrane Type	Contact Angle (degree)	Std
PAA[1]	53.76	3
PAA-CS[1a]	48.47	2
PAA-GA[1]	71.68	4
PAA-CS-GA[1a]	70.40	4
PAA-CS-GA[1b]	65.95	5
PAA-CS[2a]	46.84	3

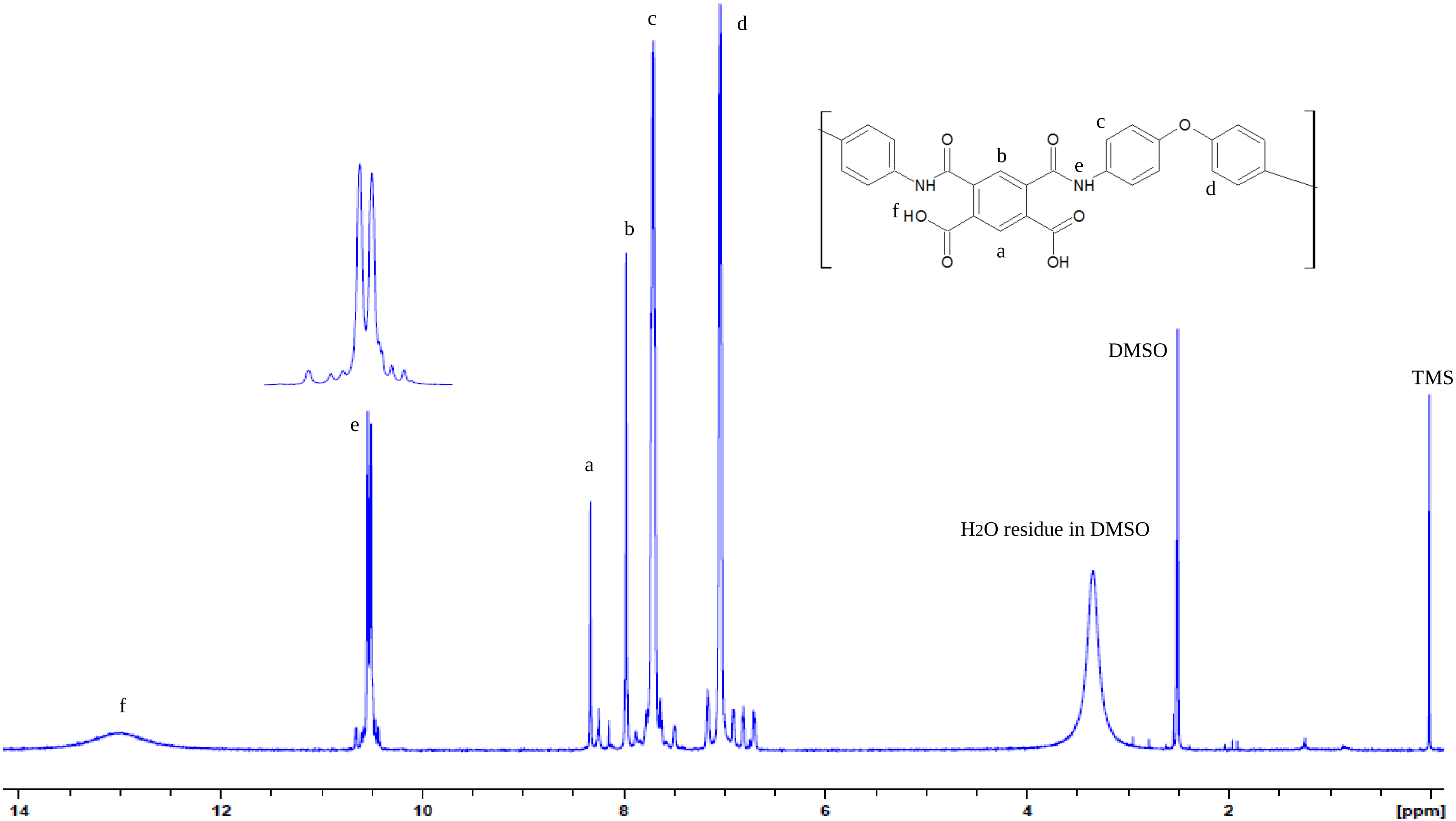
(1) 0.32 M PAA; (2) 0.25 M PAA; (a) CS, 2mg/mL and (b) CS, 7 mg/mL. Temperature during the all measurements was ~ 22 ºC.

BINGHAMTON UNIVERSITY
STATE UNIVERSITY OF NEW YORK

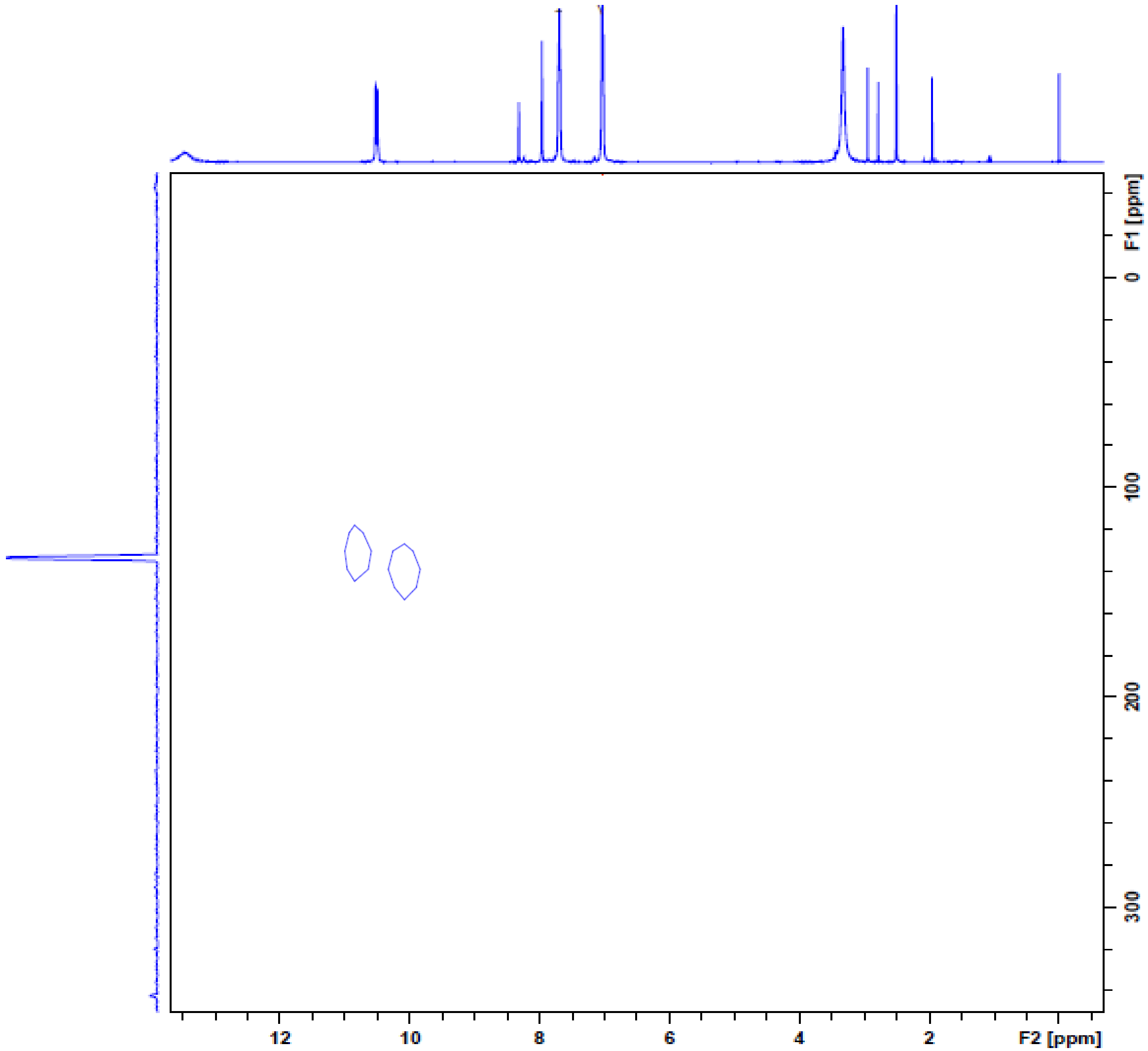
Electrochemical Characterization



Nuclear Magnetic Resonance

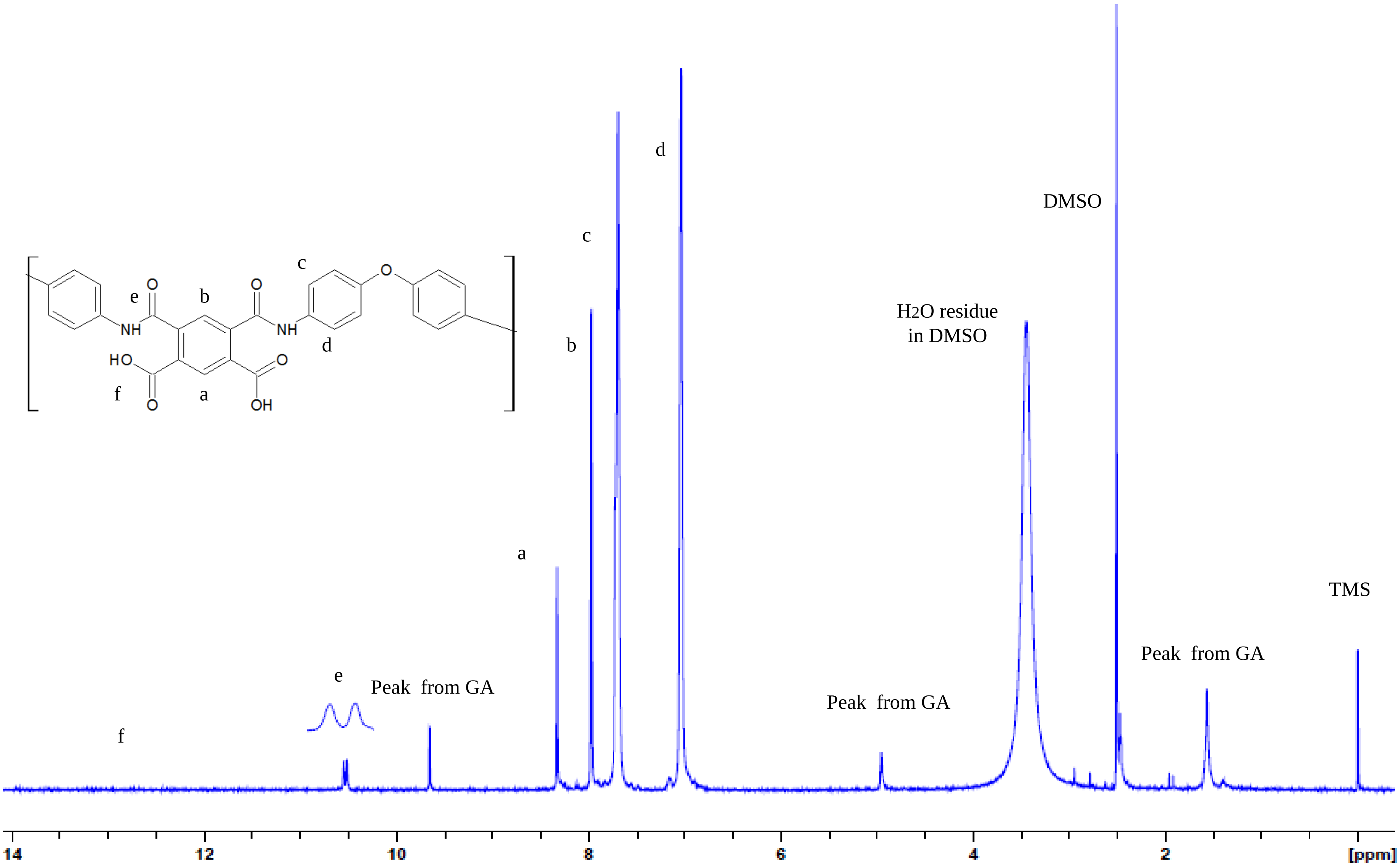


^{1}H ^{15}N HSQC NMR of PAA



BINGHAMTON
UNIVERSITY
STATE UNIVERSITY OF NEW YORK

NMR of PAA-GA



O
O
O
e
b
c
NH
NH
d
HO
O
f
a
O
OH
a
b
c
d
DMSO
H2O residue
in DMSO
TMS
e
Peak from GA
Peak from GA
Peak from GA
f
14
12
10
8
6
4
2
[ppm]

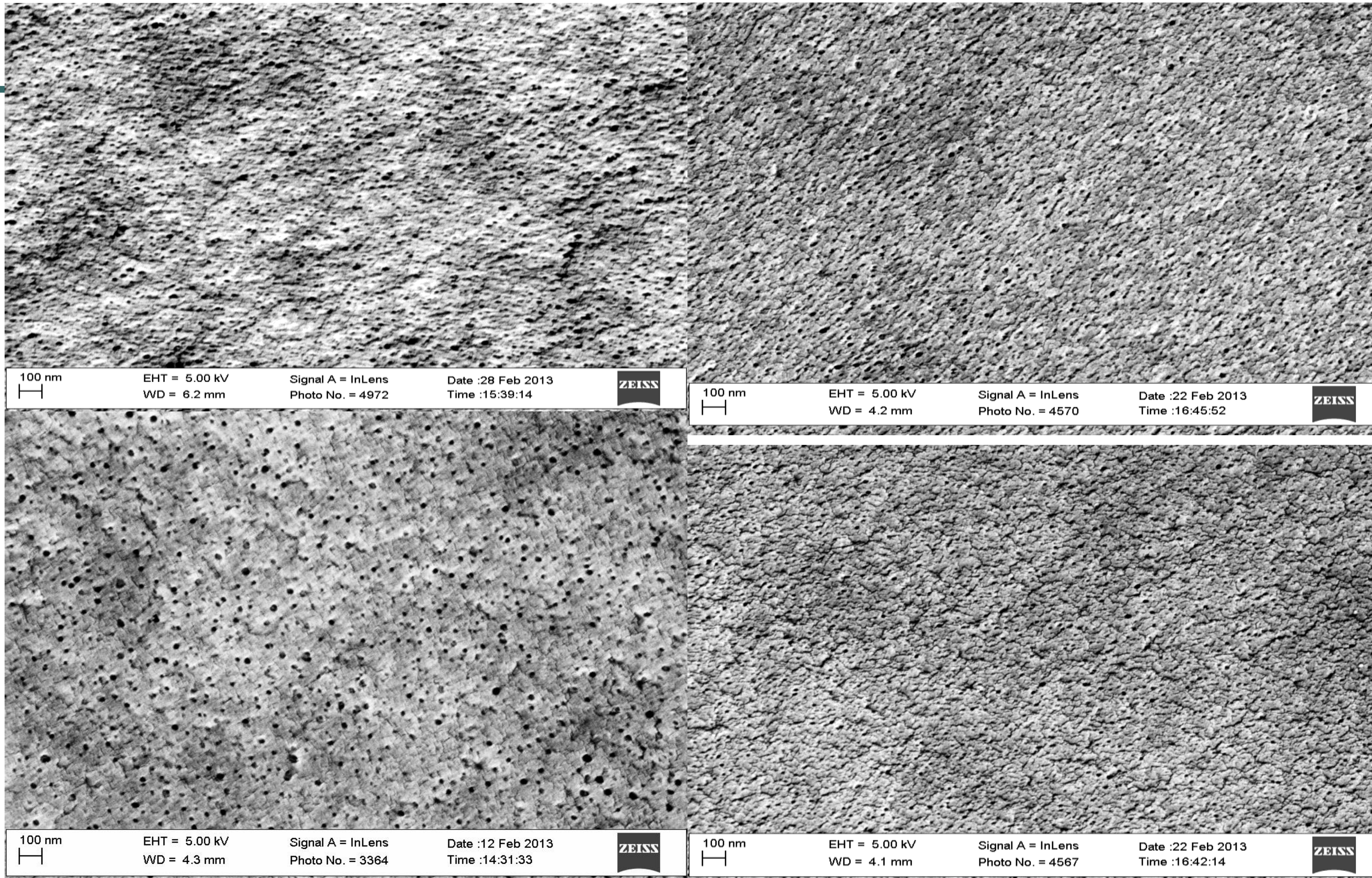
Solvent resistance of PAA membranes

Solvent	*PAA*	*PAA-CS*	*PAA - GA*	*PAA-CS-GA*
pH 9.0 50 mM PBS	Yes[a]	Yes[a]	No[b]	No[b]
pH 4.5 50 mM Acetate	Yes[a]	Yes[a]	No[b]	No[b]
Mueller-Hinton Broth	Yes[c]	Yes[c]	No[e]	No[e]
Hexan	No[b]	No[b]	No[b]	No[b]
Acetone	B	B	No[b]	No[b]
Ethanol	B	B	No[b]	No[b]
Dimethylformamide	Yes[c]	Yes[c]	Yes[c]	Yes[c]
Tetrahydrofurane	No[b]	No[b]	No[b]	No[b]
Dichlorometane	No[b]	No[b]	No[b]	No[b]
DMSO	Yes[d]	Yes[d]	Yes[d]	Yes[d]
Chloroform	No[b]	No[b]	No[b]	No[b]

BINGHAMTON
UNIVERSITY
STATE UNIVERSITY OF NEW YORK

Surface comparison of PAA membranes

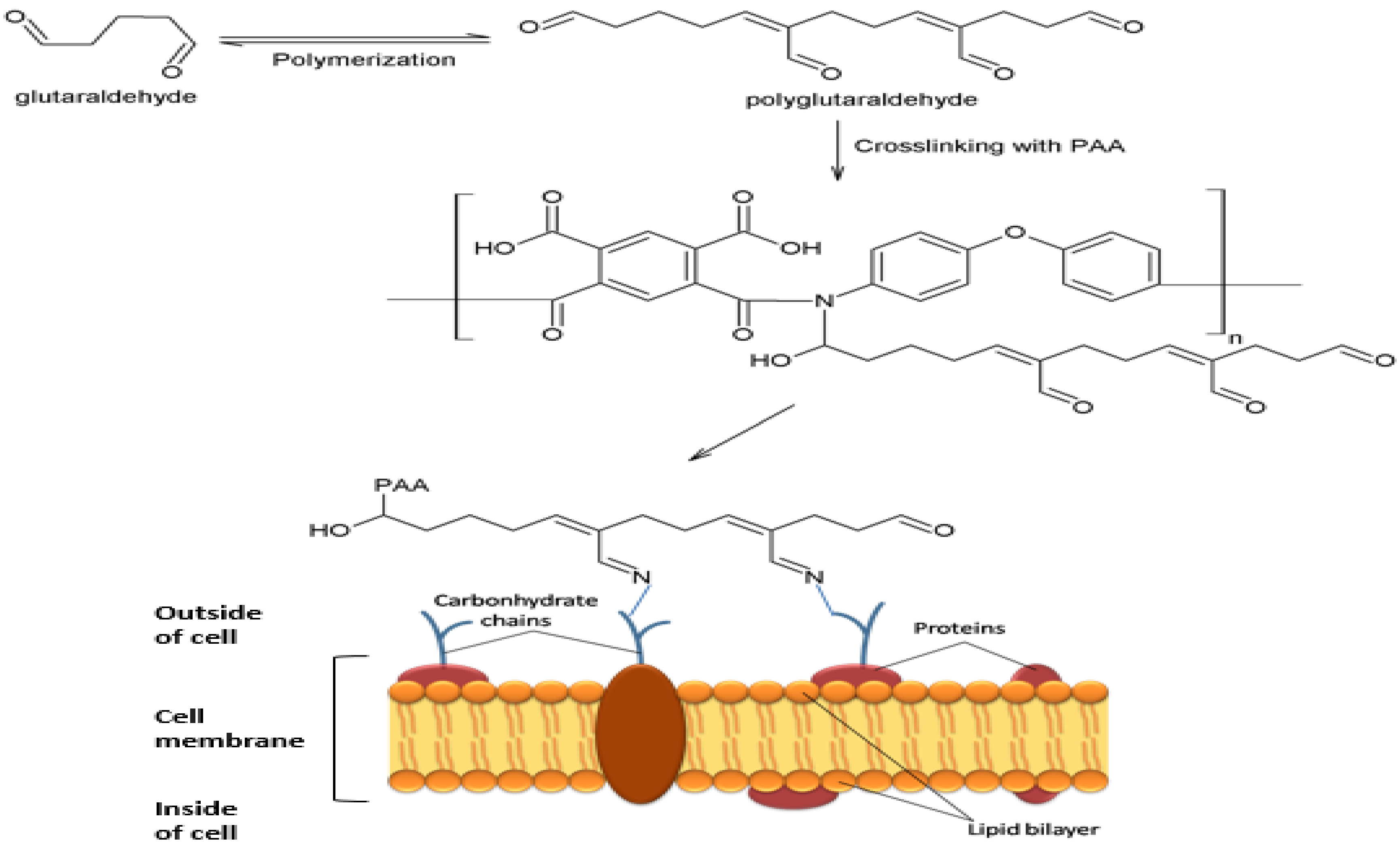
[a] [b] [c] [d]



SEM images of PAA and functionalized membranes at a magnification of 100000x. ***a.*** *PAA membrane;* ***b.*** *PAA-GA membrane; c. PAA-CS membrane;* ***d.*** *PAA-CS-GA membrane.*

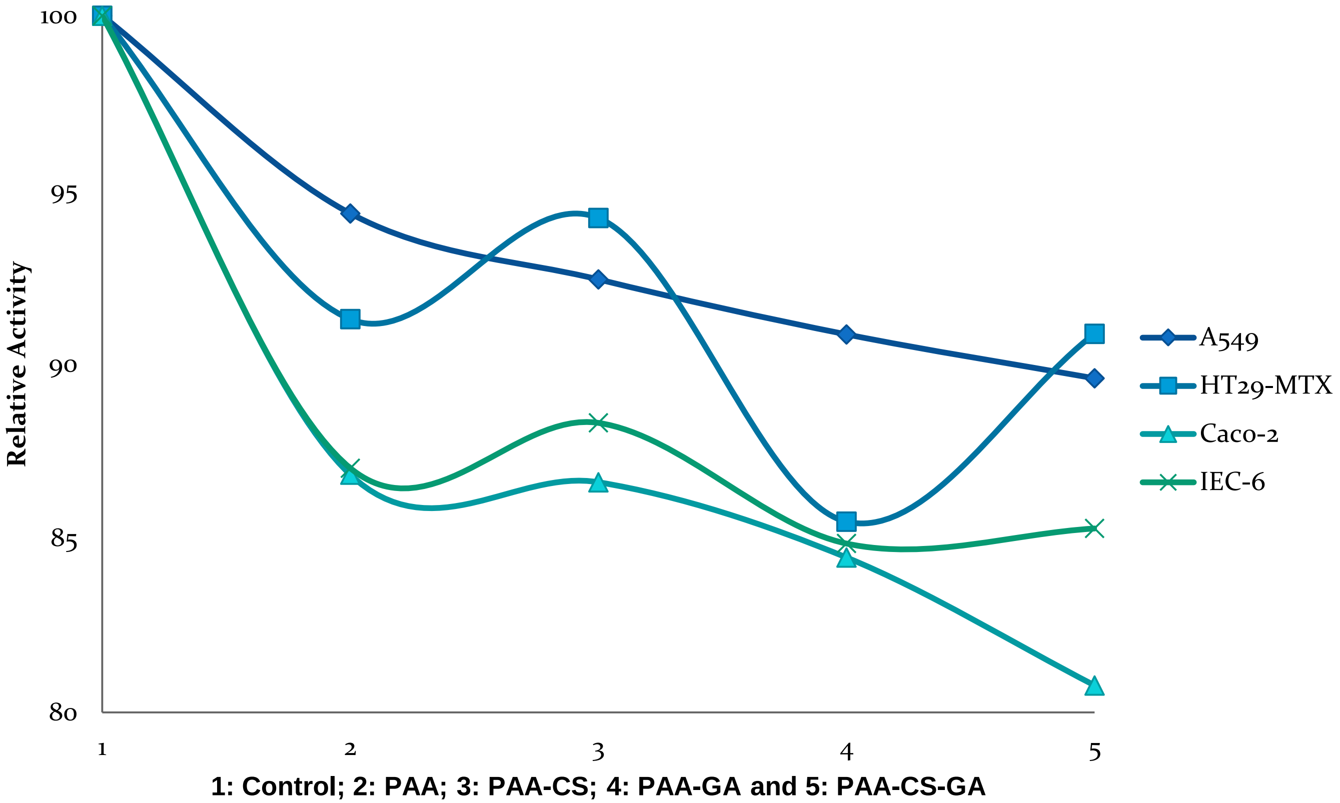
BINGHAMTON UNIVERSITY
STATE UNIVERSITY OF NEW YORK

Anti-microbial action of PAA-GA and PAA-CS-GA



Yazgan I, Sadik et al, Journal of Membrane Science 2014

Cytotoxicity Characterization



Degradation of PAA polymers

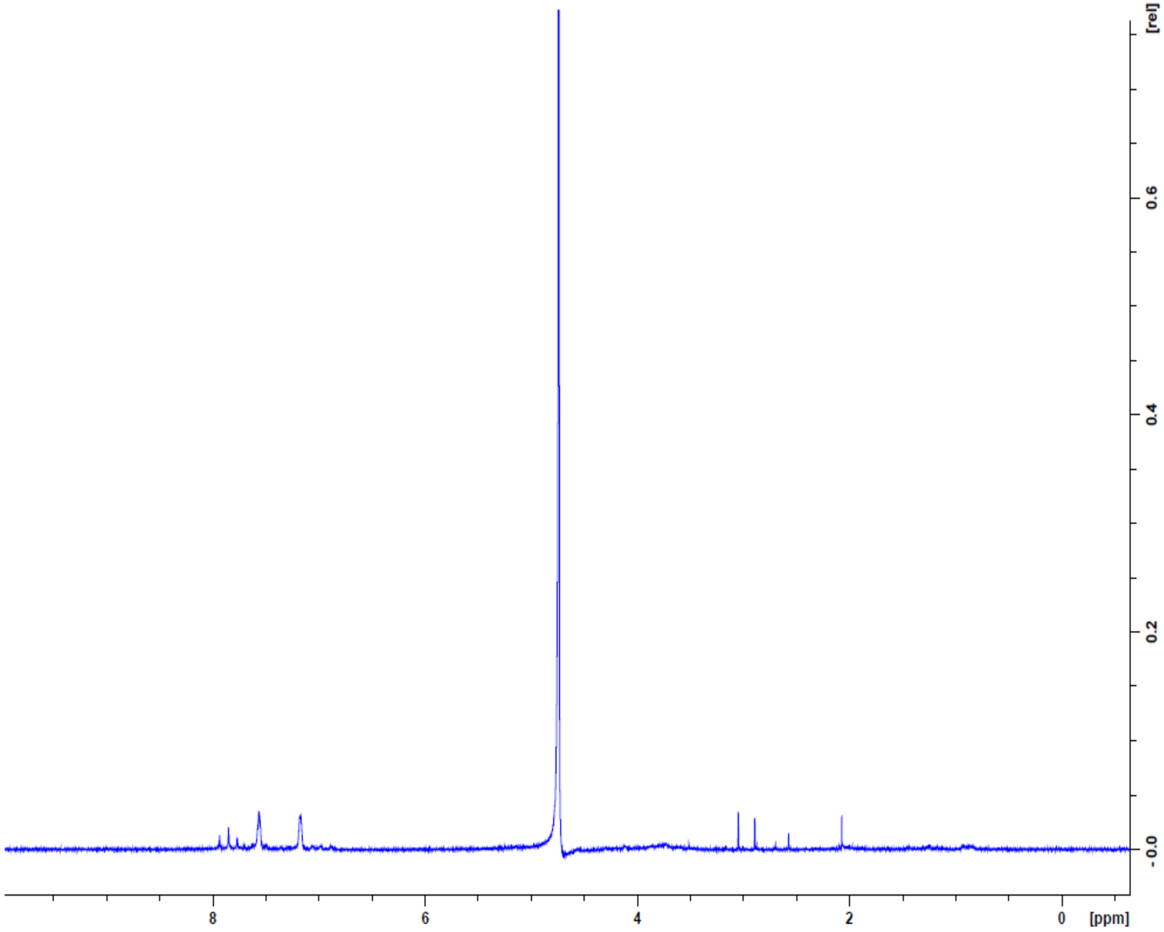
Spoiled stick [Elm tree (*Ulmus Americana*)]

Transfer of mix-microbial culture

Chemical Processes for a Sustainable Future, eds. T. M. Letcher, J. L. Scott and D. Patterson, Royal Society of Chemistry, Cambridge, UK, **2014**, 27 chapters, pages, ISBN: 978-1-849739757

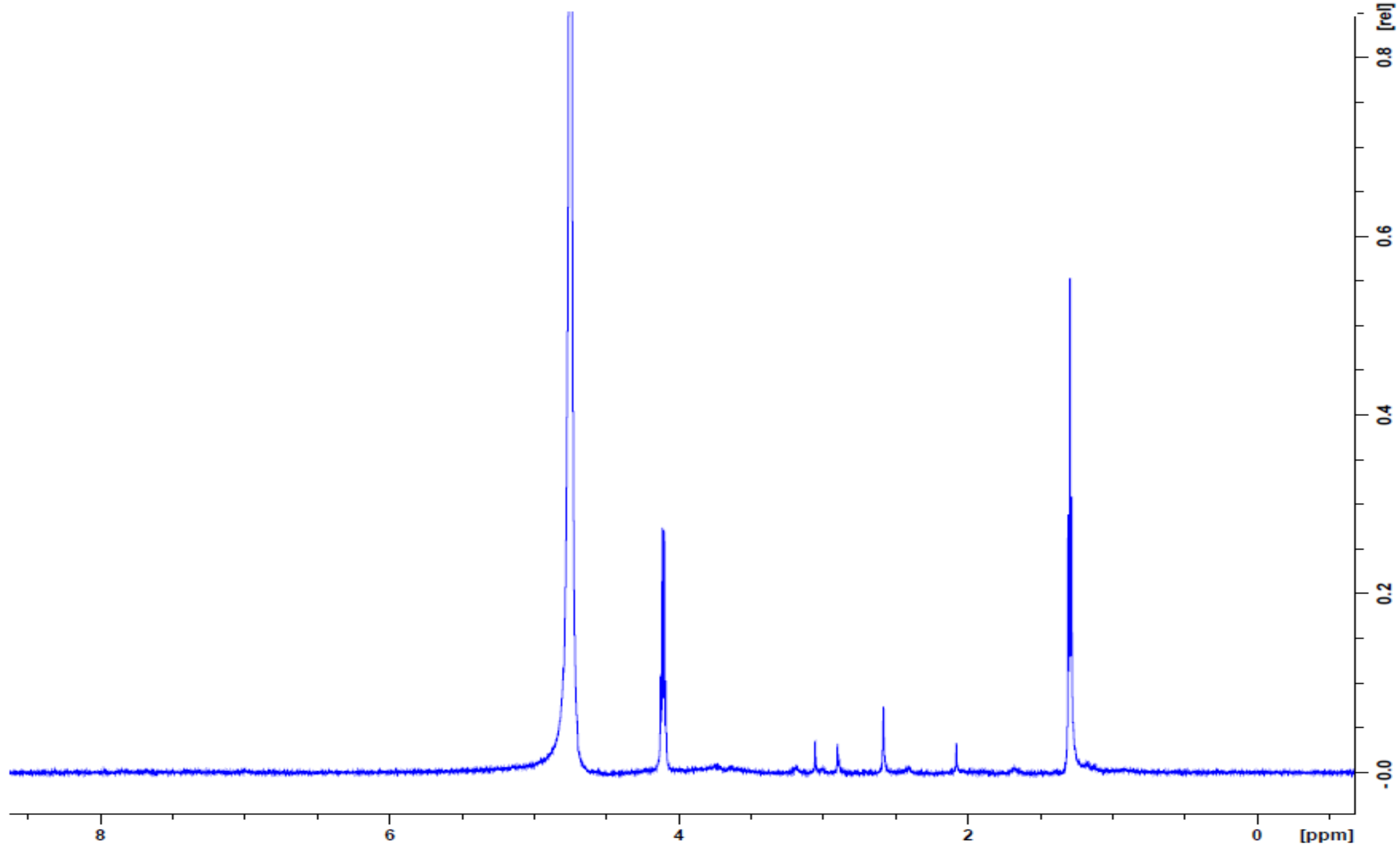
BINGHAMTON UNIVERSITY
STATE UNIVERSITY OF NEW YORK

20th day NMR from medium



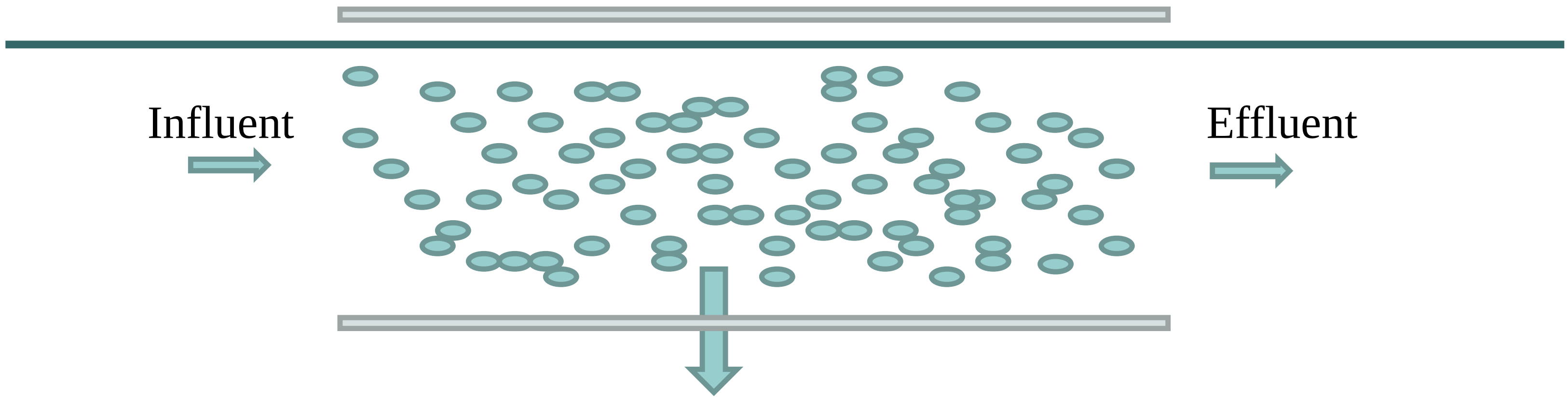
BINGHAMTON
UNIVERSITY
STATE UNIVERSITY OF NEW YORK

35th day NMR from the medium



BINGHAMTON
UNIVERSITY
STATE UNIVERSITY OF NEW YORK

Disinfection of drinking water

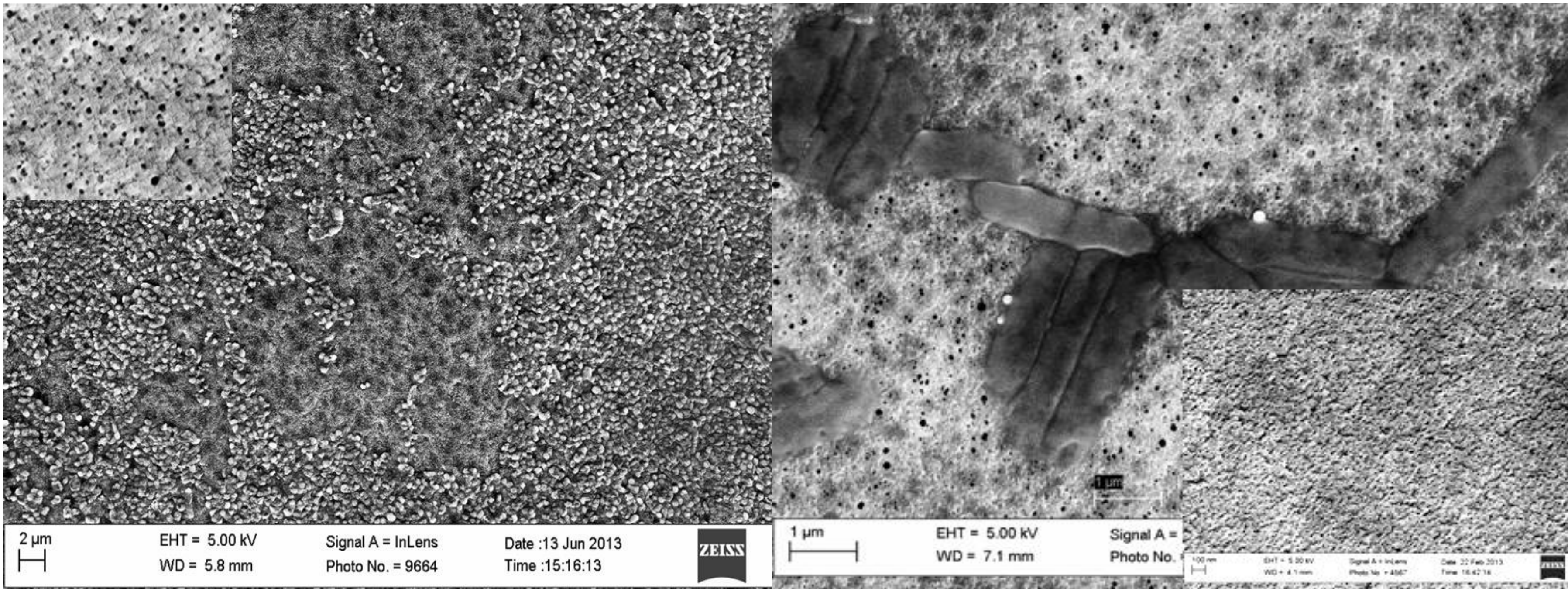


Sample volume (mL)	Amount of spiked microorganisms (cfu/mL)	Amount of total microbial residue after filtration (cfu/mL)	% Disinfection	Membrane Type Employed
500	3 x10^8	none	3 x10^8	PAA- GA
1000	3 x10^8	none	3 x10^8	PAA-CS-GA
1500	3 x10^8	none	3 x10^8	PAA-CS-GA

Sadik et al, Journal of Membrane Science, Volume 472, 15 December 2014, Pages 261-271

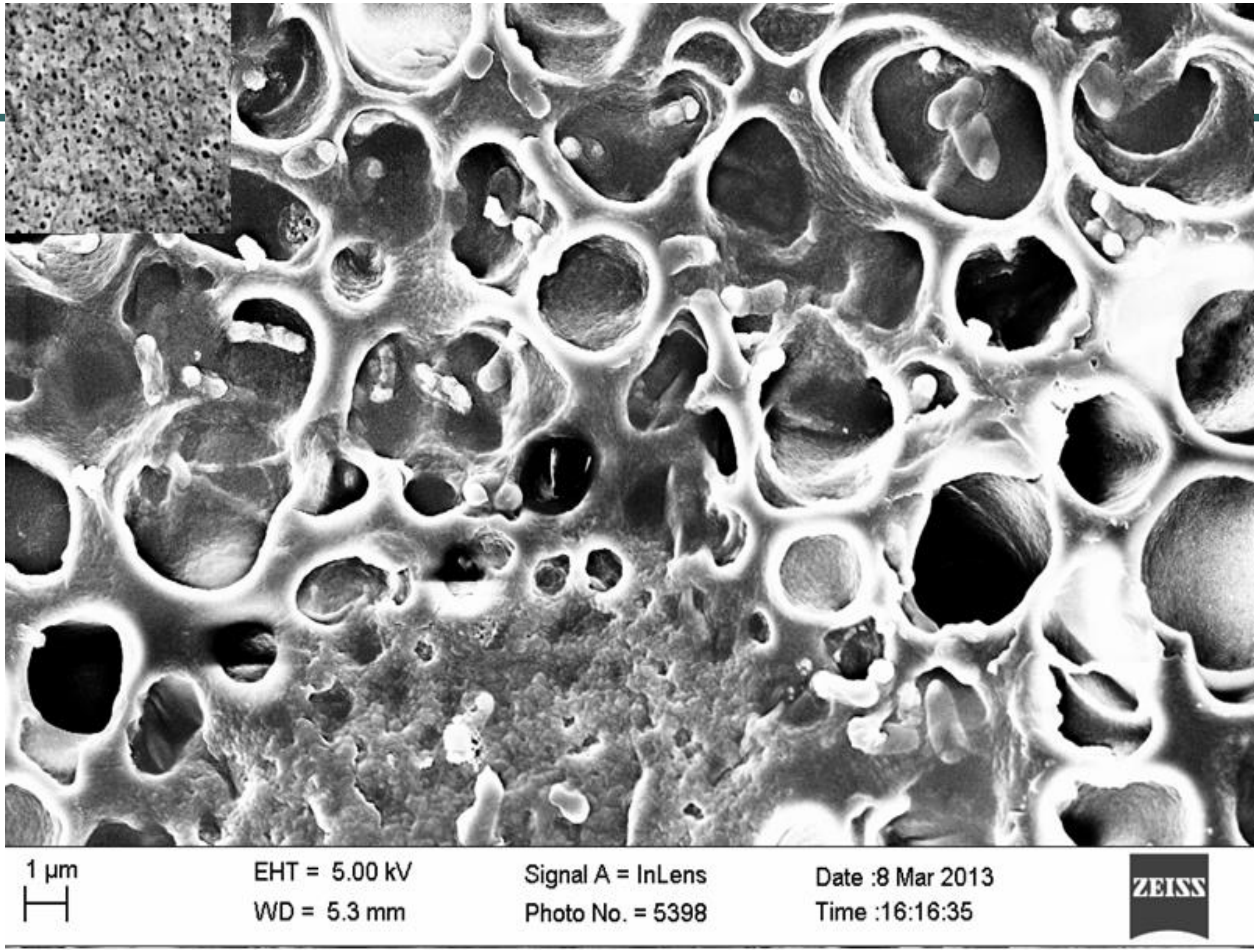
Chemical Processes for a Sustainable Future, eds. T. M. Letcher, J. L. Scott and D. Patterson, Royal Society of Chemistry, Cambridge, UK, **2014**, 27 chapters, pages, ISBN: 978-1-849739757

Post-filtration SEM image of PAA-CS-GA



GA treated PAA-CS and PAA did not lose their surface integrity and pore-size distribution for disinfection of 1000 mL tap water containing 3 e8 Staphylococcus epidermidis, Escherichia coli and *Citrobacter frenduii*

Post-filtration SEM image of PAA-CS



10 mL tap water containing 1 e8 E.coli filtrated via dead-end filtration

Conclusion and Outlook

- PAA membranes have been successfully synthesized and applied to water purification
- Potential exists for large scale disinfection of drinking water
- Characterization of the microorganisms in responsible to PAA degradation
- PAA membranes are biodegradable and non-cytotoxic.

PAA based membrane chromatography [PMC] microbial filtration

Acknowledgement

- Dr. Jurgen Schulte for evaluation of NMR data
- Prof. Gretchen Mahler for supplying Caco-2 and HT29-MTX cell lines

THANK YOU

?

BINGHAMTON UNIVERSITY
STATE UNIVERSITY OF NEW YORK

U.S. EPA - Science To Achieve Results (STAR) Program
Grant #

DTRALink

BINGHAMTON UNIVERSITY

BINGHAMTON
UNIVERSITY
State University of New York

Acknowledgements

NSF

Defense Threat Reduction Agency
DTRALink

New York State Department of
Environmental Conservation

This research is funded by
U.S. EPA - Science To Achieve Results (STAR) Program
Grant #

National Institute of
Standards and Technology NIST

IEEC
Integrated Electronics Engineering Center
STATE UNIVERSITY OF NEW YORK

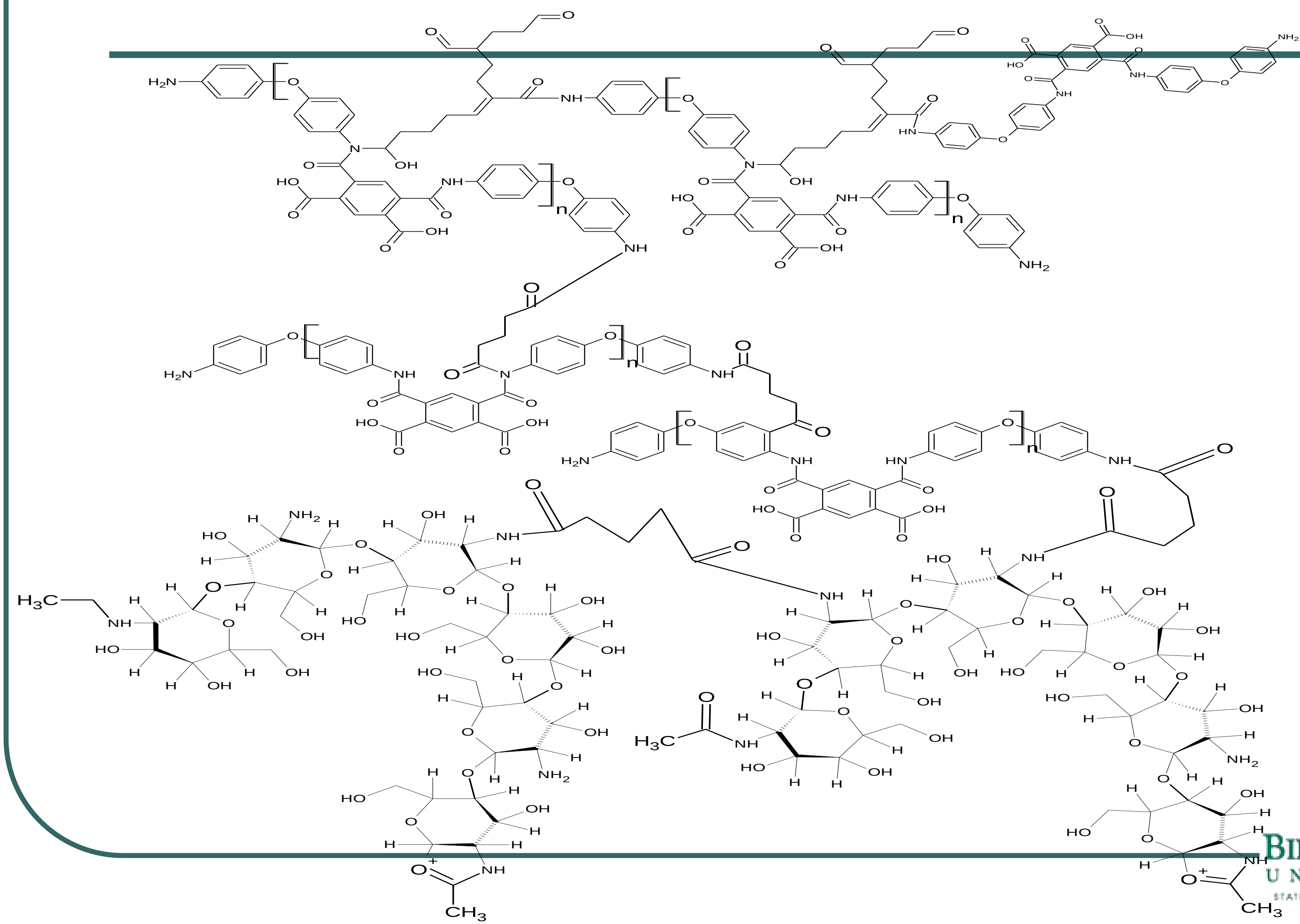
Cost of starting materials used for the synthesis of PAA and PAA-CS membranes

Material/Catalog number	Cost in $ from Sigma Aldrich
Pyromelliticdianhydrate (PMDA), 412287	127.0/500G
N,*N*-Dimethylacetamide (DMAC), 271012	134.50/2L
Chitosan (CS), 448869	46.70/50G
Glutaraldehyde solution (GA), G7651	224.0/100 mL
4,4'-Oxydianiline (ODA), 516805	162.50/500G

Material	PAA-GA	PAA-CS-GA
ODA	2.08	2.08
PMDA	2.1	2.1
DMAC	6.72	6.72
Chitosan	-	0.093
Total cost	12.47$/100 mL viscous PAA solution	12.51 $/100 mL viscous PAA-CS solution
GA	1.12/water bath	1.12/water bath
Membrane cost	1.08 $/L water	0.19 $/L water

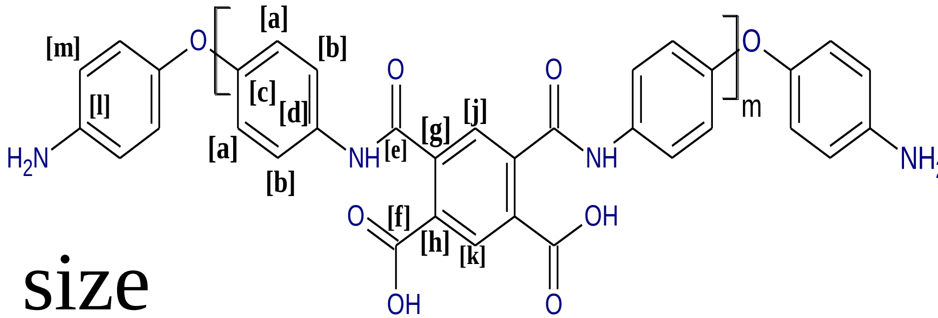
Membrane cost per liter tap water disinfection was calculated in two steps. (1) In order to prepare 120 x 18 x 0.30 mm membranes 3 mL PAA viscous solution was used, so its expense as added to the cost of GA. (2) Cost of the membrane is then divided to the volume of disinfected tap water, in which re-usability was taken into account.

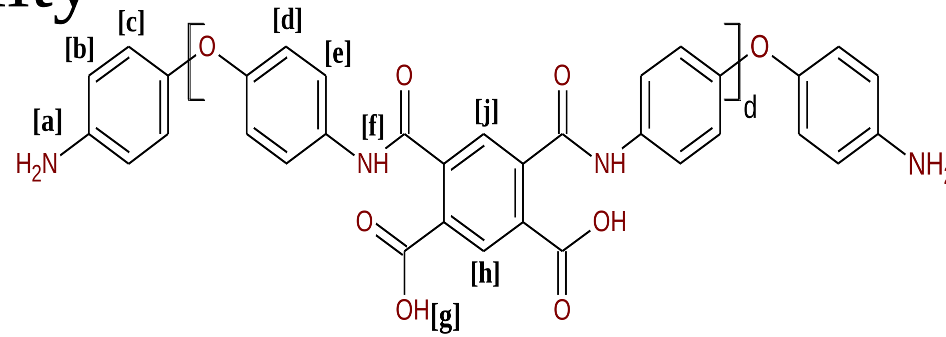
Possible PAA-GA-CS structure



Why PAA?

- Easy to modify
  - Non-soluble membranes
- Controllable nano-pore size
- Potency of biodegradability
- Free from cytotoxicity
- Conductivity





Sadik et al. Langmuir **2010**, 26 (17), 14194–14202