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14. ABSTRACT
This report describes the progress made under the auspices of the funded project. Specifically, developments have centered around four issues: 1. Models and simulations which address the impact of role of polymer-surface interfacial interactions upon the macroscopic properties;

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Report Title

Multiscale Simulations of Barrier and Aging Properties of
Polymer Nanocomposites

ABSTRACT

This report describes the progress made under the auspices of the funded project. Specifically, developments have centered around four issues:

1. Models and simulations which address the impact of role of polymer-surface interfacial interactions upon the macroscopic properties;

2. Development of a new computational method capable of predicting the barrier properties of polymer membranes;

3. Development of a coarse-grained computational method to address the physical mechanisms underlying the barrier properties of polymer nanocomposite membranes;

4. Atomistic and quantum mechanical investigation of the transport properties of polymer membranes proposed for use in fuel cell applications.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>   <u>Paper</u>

08/27/2012 7.00 Benjamin Hanson, Venkat Ganesan, Victor Pryamitsyn. Coarse-Grained Simulations of Penetrant Transport in Polymer Nanocomposites,
Macromolecules, (12 2011): 0. doi: 10.1021/ma201712j

08/27/2012 14.00 Venkat Ganesan, N. Arun Kumar, Victor Pryamitsyn. Blockiness and Sequence Polydispersity Effects on the Phase Behavior and Interfacial Properties of Gradient Copolymers,
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08/27/2012 13.00 Sung Hyun Han, Victor Pryamitsyn, Dusik Bae, Jongheon Kwak, Venkat Ganesan, Jin Kon Kim. Highly Asymmetric Lamellar Nanopatterns via block copolymer blends capable of hydrogen bonding,
ACS Nano, (08 2012): 0. doi: 10.1021/nn3025089

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Soft Matter, (08 2012): 6471. doi: 10.1039/c2sm25577d

08/27/2012 11.00 Victor Pyramitsyn, Colleen Bertoni, Manas Shah, Venkat Ganesan. Mechanisms Underlying Ion Transport in Lamellar Block Copolymer Membranes,
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08/27/2012 10.00 David Trombly, Victor Pryamitsyn, Venkat Ganesan. Surface Energies and Self-Assembly of Block Copolymers on Grafted Surfaces,
Physical Review Letters, (09 2011): 148304. doi: 10.1103/PhysRevLett.107.148304

08/27/2012 9.00 David M. Trombly, Victor Pryamitsyn, Venkat Ganesan. Self-Assembly of Diblock Copolymer on Substrates Modified by Random Copolymer Brushes,
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08/27/2012 8.00 Ben Hanson, Victor Pryamitsyn, Venkat Ganesan. Computer Simulations of Gas Diffusion in Polystyrene–C,
The Journal of Physical Chemistry B, (01 2012): 95. doi: 10.1021/jp209294t

10/29/2013 16.00 Venkat Ganesan, Jin Kon Kim, Victor Pryamitsyn, Sung Hyun Han. Curvature Modification of Block Copolymer Microdomains Using Blends of Block Copolymers with Hydrogen Bonding Interactions,
Macromolecules, (11 2012): 8729. doi: 10.1021/ma301402n

10/29/2013 17.00 Chetan V. Mahajan, Venkat Ganesan. Influence of Hydrogen Bonding Effects on Methanol and Water Diffusivities in Acid–Base Polymer Blend Membranes of Sulfonated Poly(ether ether ketone) and Base Tethered Polysulfone,
The Journal of Physical Chemistry B, (05 2013): 5315. doi: 10.1021/jp3121512

10/29/2013 18.00 Venkat Ganesan, Victor Pryamitsyn. Effect of confinement on polymer-induced depletion interactions between nanoparticles,
The Journal of Chemical Physics, (06 2013): 234905. doi: 10.1063/1.4809990

10/29/2013 19.00 Dylan Kipp, Venkat Ganesan. A kinetic Monte Carlo model with improved charge injection model for the photocurrent characteristics of organic solar cells,
Journal of Applied Physics, (06 2013): 234502. doi: 10.1063/1.4811337

10/29/2013 20.00 Venkat Ganesan, Thomas Lewis. Interactions between Grafted Cationic Dendrimers and Anionic Bilayer
Membranes,
The Journal of Physical Chemistry B, (08 2013): 9806. doi: 10.1021/jp4053049

TOTAL: **13**

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>   <u>Paper</u>

08/23/2011 2.00 Sung Hyun Han, Jin Kon Kim, Victor Pryamitsyn, Venkat Ganesan. Phase Behavior of Binary Blends of
Block Copolymers Having Hydrogen Bonding,
Macromolecules, (06 2011): 0. doi: 10.1021/ma200747d

08/23/2011 3.00 David M. Trombly, Victor Pryamitsyn, Venkat Ganesan. Interfacial properties of statistical copolymer
brushes in contact with homopolymer melts,
The Journal of Chemical Physics, (04 2011): 0. doi: 10.1063/1.3575182

08/27/2012 15.00 Benjamin Hanson, Victor Pryamitsyn, Venkat Ganesan. Molecular mass dependence of point-to-set
correlation length scale in polymers,
Journal of Chemical Physics, (08 2012): 84904. doi:

TOTAL: **3**

Number of Papers published in non peer-reviewed journals:

(c) Presentations

1. "A Dynamic Monte Carlo Model with an Improved Charge Injection Mechanism for the Photocurrent Generation of Organic Solar
Cells," Dylan Kipp and Venkat Ganesan, March Meeting of the American Physical Society, Baltimore (2013).
2. "Complexation Between Weakly Basic Dendrimers and Linear Polyelectrolytes: Effects of Chain Stiffness, Grafts, and pOH," Thomas
Lewis, Gunja Pandav, Ahmad Omar and Venkat Ganesan, March Meeting of the American Physical Society, Baltimore (2013).
3. "Multi-body effects in Charged Colloids - Polyelectrolyte systems," Victor Pryamitsyn and Venkat Ganesan, March Meeting of the
American Physical Society, Baltimore (2013).
4. "Effect of Fluctuation on Order-Disorder Transition in Polydisperse Block Copolymer Melts," Gunja Pandavr and Venkat Ganesan,
March Meeting of the American Physical Society, Baltimore (2013).
5. Equilibrium and dynamical coarse-graining of polymer nanoparticle mixtures, CECAM International Workshop on Coarse-graining
multicomponent soft matter systems: equilibrium and dynamics, Mainz, Germany, August 2013.
6. Influence of sequence distribution effects on the phase behavior and interfacial properties of random copolymers, Plenary talk at the
Annual Meeting of American Institute of Chemical Engineers, Pittsburgh, November 2012.

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received   Paper

TOTAL:

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Peer-Reviewed Conference Proceeding publications (other than abstracts):

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TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received   Paper

08/23/2011 4.00 Victor Pryamitsyn, Benjamin Hanson, Venkat Ganesan. Coarse-grained Simulations of Penetrant
Transport in Polymer Nanocomposites,
(submitted) (07 2011)

08/23/2011 5.00 Ben Hanson, Victor Pryamitsyn, Venkat Ganesan. Simulation of Gas Diffusion In Polystyrene C60
Fullerene Nanocomposites Using Time Extending Kinetic Monte Carlo,
(submitted) (08 2011)

08/23/2011 6.00 David M. Trombly, Victor Pryamitsyn, Venkat Ganesan. Surface Energies and Self-Assembly of Block
Copolymers on Grafted Surfaces,
(submitted) (08 2011)

TOTAL: **3**

Number of Manuscripts:

Books

<u>Received</u>   <u>Paper</u>

TOTAL:

Patents Submitted

Patents Awarded

Awards

1. Fellow of American Physical Society (2013).
2. Kobe Professorship in Chemical Engineering, UT Austin (2013).
3. Moncrief Faculty Grand Challenge Award (2013).

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Gunja pandav	0.10	
Thomas Lewis	0.25	
David Trombly	0.25	
Chetan Mahajan	0.10	
FTE Equivalent:	**0.70**	
Total Number:	**4**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Benjamin Hanson	0.75
Victor Pryamitsyn	0.25
FTE Equivalent:	**1.00**
Total Number:	**2**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Venkat Ganesan	0.50	
FTE Equivalent:	**0.50**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Ahmad Omar	0.10	
FTE Equivalent:	**0.10**	
Total Number:	**1**	

Student Metrics
This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 1.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 1.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 1.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 1.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 1.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME
Thomas Lewis
Total Number: 1

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See attachment

Technology Transfer

Final Report: 2012 - 2013

1. Summary of Broad Objectives

This project proposes the development of a multiscale computational approach to predict the barrier and aging properties of polymer-nanoparticle composites (PNCs). The specific objectives are:

(i) Develop and apply a new multiscale computer simulation approach to predict the barrier and selectivity properties of polymer nanocomposite membranes. This will build upon our recent work on coarse-graining techniques for PNC systems, but extend it in new directions by rendering it a predictive tool for characterizing penetrant transport in PNC membranes.

(ii) Develop and apply a new multiscale computer simulation approach capable of characterizing the aging properties of polymer nanocomposites. This effort is motivated by recent work from our group, but shares many components with objective 1. Our intent was to use the results of such computer simulations to develop fundamental models which can facilitate modeling and prediction of the aging properties of polymer nanocomposites and confined films.

We proposed to address the above features by developing multiscale simulation approaches which use a combination of molecular/atomistic simulations, mesoscale simulations and macroscale models to predict both the dispersion state and macroscopic properties of PNCs.

In this period of the annual report, scientific progress has been achieved in three broad directions:

1. Development of a new computational method capable of predicting the barrier properties of polymer membranes: We extended our time-extending simulation method to study penetrant transport in glassy polymer matrices. This methodology was used to study: (i) The effect of nanoparticles on the diffusion of Lithium ions through PEO matrices.

2. Atomistic and quantum mechanical investigation of the transport properties of polymer membranes proposed for use in fuel cell applications. This project is broadly related to (2) above, but includes the possibility for proton hopping and acid-base chemical equilibria.

3. Cationic dendrimers have shown great promise in drug and gene therapy applications. Despite the advantages realized through positively charged dendrimers, a number of studies

1

have noted that the non-specific electrostatic binding to charged lipid head groups of cellular membranes may contribute to dendrimer cytotoxicity, and such effects have been noted to increase with dendrimer size, charge density, and concentration. Despite a number of efforts, there is still not full clarity on the physics and parameters governing dendrimer-membrane interactions and the role of grafts in modulating such interactions. Motivated by the above considerations, in this study we developed a coarse-grained model of grafted, charged dendrimers interacting with anionic membranes.

2. *Conductivity of polymer membranes using time-extending simulations*

Electrochemical devices such as batteries and fuel cells have recently become popular in the quest for clean and sustainable energy sources. Electrolytes that facilitate ion transport between electrodes are key components in such devices, and polymeric membrane materials have emerged as attractive candidates for such applications.[1–6,6–12] However, high ionic conductivities in polymeric materials are often obtained in rubbery polymers which lack the requisite mechanical strength for solid state batteries.[13] In an effort to enhance the mechanical properties of such polymer membranes, a variety of strategies have been explored, such as cross-linking of the conductive homopolymers, using diblock copolymers etc.[14–23] In such contexts, interest has recently arisen in the strategy of using "nanocomposite" membranes, which contain nanoscale inorganic fillers dispersed in the polymer matrix.[24–31] A number of studies have demonstrated that the addition of ceramic particles having nanoscale dimensions and suitable surface characteristics can improve properties such as anodic stability,[29] the low temperature conductivity and the cyclability of the polymer matrix.[32–36] Such demonstrations have provided a strong motivation for understanding of the influence of nanoparticles on the electrochemical properties of polymeric electrolytes.

This specific work was motivated by the influence of nanoscopic filler particles upon the low temperature conductivity of the polymer matrix. For instance, Croce *et al.*[27] considered TiO_2 particles dispersed in a poly(ethylene-oxide) (PEO) matrix and demonstrated an increased ionic conductivity relative to the pure polymer matrix. Such results were rationalized by suggesting that the addition of nanoparticles suppresses the crystallization of the polymer matrix to promote the local mobility of the polymers.[29,37,38] On the other hand, some experiments have noted that conductivity enhancements in composite polymer electrolytes can

2

occur even at temperatures above the melting point of the polymer, which suggests that the physical mechanism underlying conductivity enhancements cannot be attributed solely to the suppression of crystallization.[25,29,39,40] Moreover, in some cases, lowering of conductivity has been observed upon the addition of nanoparticle fillers.[37,41] Such contradicting results motivate the questions, "What are the mechanisms underlying the ionic conductivities of polymer nanocomposites?," "Do ion conductivities in polymer nanocomposites always correlate with the influence of the fillers on the polymer mobilities?," and "What is the role of nanoparticle-induced modifications in polymer conformations in influencing ion mobilities?"

In Fig. 1, we present results for the lithium ion diffusivities, D, in PEO matrices as a function of particle loading for three different temperatures. We observe that there is a monotonic increase in the ion mobilities with increasing system temperature. Such a behavior can be understood as a consequence of the increase in polymer mobilities with increasing temperature. More pertinently, we observe that at a specified temperature, the lithium diffusivity decreases monotonically with the addition of nanoparticles. We note that in general the addition of nonconducting nanoparticle obstacles is expected to block conducting pathways and lead to diminished ion diffusivities. However, the mobility reductions expected from such effects are expected to be less than 10% for even the highest particle volume fraction considered in our study (which was of the order of 5%). It can be seen that the mobility reductions in our system significantly exceed the magnitudes expected from such obstructional effects, and indicates nontrivial mechanisms underlying the influence of nanoparticles.

To probe the correlation between the lowering of ionic mobilities (Fig. 1) and the polymer segmental relaxation times, in Fig. 2 we display a direct comparison of the ionic diffusivities with the inverse relaxation times. While the diffusivities are seen to deviate from the behavior expected from Stokes-Einstein like relationship ($D \propto \tau^{-1}$), nevertheless, for both lithium concentrations it is seen that the ionic mobilities are strongly correlated to the modified polymer segmental relaxation times. Such a result suggests that the impact of nanoparticles upon the ionic mobilities arises primarily as a consequence of the influence of the former upon the polymer segmental dynamics.

In summary, we presented results of atomistic MD simulations based on multibody polarizable force fields which showed that the addition of nanoparticles to polymer matrices leads to significant changes in polymer conformations and their dynamics. However, there
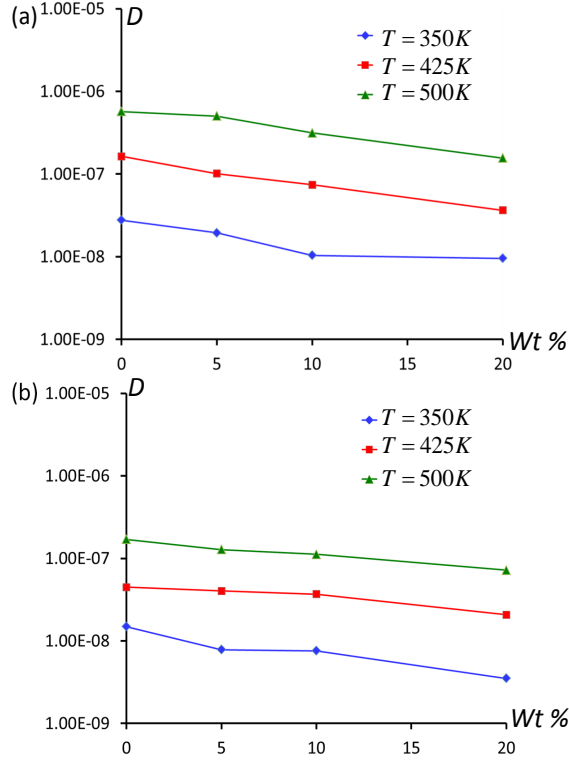
3

FIG. 1: Diffusivities D (cm^2 s^{-1}) of Lithium ions in PEO + TiO$_2$ nanoparticle matrices as a function of weight percentage of nanoparticles: (a) EO:Li = 15:1; (b) EO:Li = 8:1. Lines are meant to be a guide to the eye.

was observed to be a strong correlation between the particle-induced modifications of the polymer conformations and the polymer segmental dynamics. As a result, ionic diffusivities followed the trends exhibited by polymer segmental dynamics. More generally, our results suggest that ionic mobilities in filled polymer systems strongly correlates with the polymer segmental dynamics when there is a strong interrelationship between polymer conformational features and their dynamics. In future studies, we plan to explore the generality of our results for other polymer-filler combinations.

• Publications Resulting: One publication in press.

3. Conductivity and transport properties of polyelectrolyte membranes

This project focuses on development of computational tools to predict the transport properties of protons in polymer membranes. Since transport of protons involve bond dissociation processes, such phenomena necessitate quantum mechanical calculations. Our goal
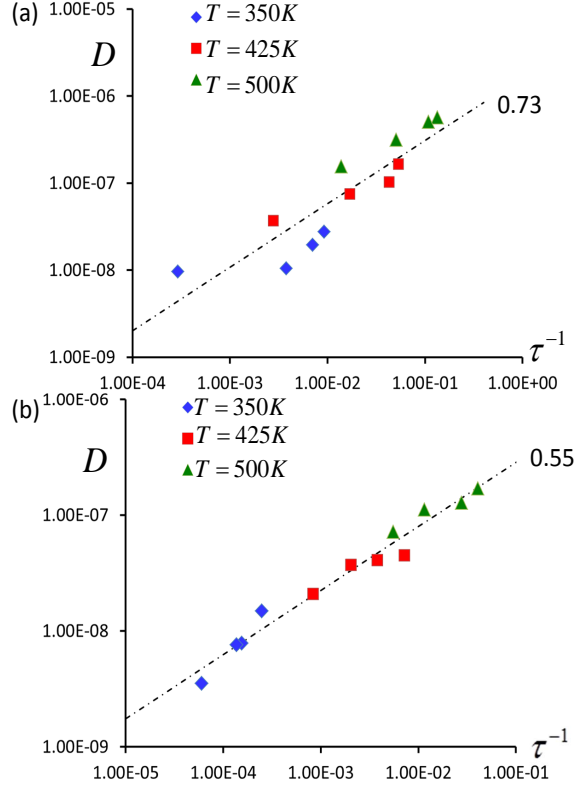
FIG. 2: Ionic diffusivities D displayed as a function of inverse of mean polymer segmental relaxation times in PEO + TiO$_2$ nanoparticle matrices as a function of weight percentage of nanoparticles: (a) EO:Li = 15:1; (b) EO:Li = 8:1. The different points correspond to the different loadings of the nanoparticles. The dotted line indicates the power law fit to the data and the numbers correspond to the exponent of such a fit.

was to develop a simulation scheme which uses quantum mechanically determined rates of proton transport within the classical simulations of penetrant transport and predict the overall conductivities of polymer membranes.

Recently acid-base polymer blend membranes are emerging as a promising class of fuel cell membranes which present opportunities for maximizing proton conductivity and high temperature dimensional stability with concomitant minimization of methanol crossover. Many features, such as strength of acid-base hydrogen bonding interactions, hydrophobicity of the base, size of the base etc. have been speculated as possible causes for their properties. However, despite the many experimental demonstrations of the novel properties of such membranes, a fundamental mechanistic understanding of the origins of the properties of such membranes is lacking. In addition to the fundamental implications, such an understanding may help in optimizing the properties of the membranes.

Using all-atom classical molecular dynamics simulations, we recently elucidated, for the first time, how hydrogen bonding interactions in such membranes affect the methanol transport in such membranes. Explicitly, we demonstrated that accounting for acid-base hydrogen bonding interactions is necessary to obtain experimentally observed trends. However, we also show that in most cases, increasing the strength of the acid-base hydrogen bonding interactions does not lead to an increase in the methanol diffusivities in such systems. The strength of the parasitic hydrogen bonding interactions is shown to correlate with the pore distribution characteristics of the membranes and thereby affect the methanol diffusivities in such systems. The relative strengths of the acid-base and parasitic hydrogen bonding interactions are in turn shown to be influenced by interplay between structure and the size of the base units. Our simulation results not only correlate qualitatively (and in many cases, quantitatively) with the experimentally-noted trends of methanol crossover characteristics of the candidate blend membranes, but also allow us to justify the experimental results noted in other systems (which were not simulated in our work).
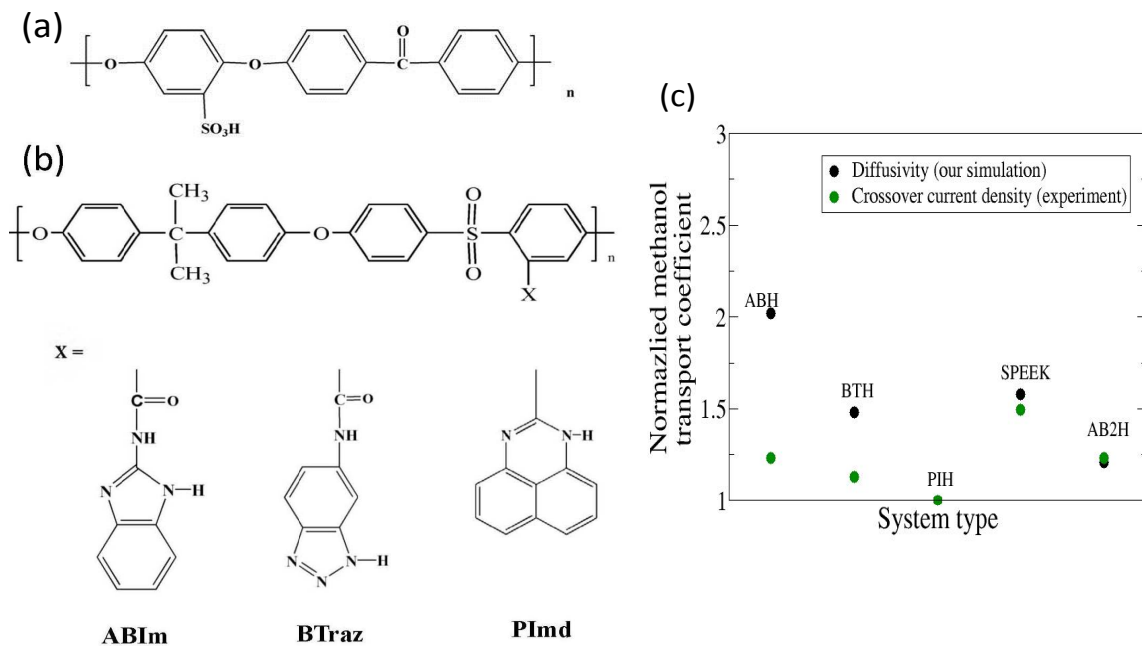

FIG. 3: (a) Structure of sulfonated subunit of SPEEK; (b) Polysulfone unit at the top with the different bases (considered in this study) at the bottom:(i) ABIm (2-amino-benzimidazole); (ii) BTraz (5-amino-benzotriazole); (iii) PImd (1-H-perimidine); (c) Comparison of normalized methanol diffusivity in our simulation to normalized methanol crossover current density in experiments in Li *at al.*.[42] Both simulated and experimental normalizations are with respect to corresponding value in PIH (or PImd) blend system.

6

• Publications Resulting: One publication.

4. *Interactions between dendrimers and lipid membranes*

Cationic dendrimers have shown great promise in drug and gene therapy applications. Despite the advantages realized through positively charged dendrimers, a number of studies have noted that the non-specific electrostatic binding to charged lipid head groups of cellular membranes may contribute to dendrimer cytotoxicity, and such effects have been noted to increase with dendrimer size, charge density, and concentration. Despite a number of efforts, there is still not full clarity on the physics and parameters governing dendrimer-membrane interactions and the role of grafts in modulating such interactions. Motivated by the above considerations, in this study we developed a coarse-grained model of grafted, charged dendrimers interacting with anionic membranes. We use such a model to study the following issues:

(i) *How do the dendrimer conformational degrees of freedom influence its interactions with and permeation through membranes?*

(ii) *How does the addition of neutral grafts affect the interactions between dendrimers and charged bilayers?*

(iii) *How does solution pH and membrane surface tension affect the interactions between dendrimers and charged bilayers?*

Our results were in qualitative agreement with observations from previous molecular dynamics simulation studies.[43,44] We observed that dendrimers undergo significant conformational changes to maximize contact between their monomers and the negatively charged lipid head groups. By performing corresponding calculations for interactions between membranes and (i) non-deformable, porous dendrimers and (ii) charged hard spheres, we were able to delineate the influences of the penetrability and deformability of the dendrimer on the PMFs for dendrimer-membrane interactions. For flexible dendrimers, there was a strong attraction seen between the dendrimer and membrane, with no energy barriers in the insertion of the dendrimer into the membrane. In contrast, the non-deformable dendrimers and charged hard spheres exhibit an energy barrier with an effective well at a finite distance from the membrane. The dendrimer-membrane attraction was seen to be strongest for the deformable dendrimers and weakest for the charged hard spheres.

The addition of neutral grafts to the dendrimer exterior was shown to affect the attraction between the dendrimer and the membrane. In general, we observed that at neutral pH, the grafted dendrimers experienced a repulsive dendrimer-membrane potential, which arose from the increase in steric repulsions between the grafts and the membrane. However, when the pH was lowered representative of the environment in the endosome, the low generation dendrimers developed an attractive well in their PMF profiles. Furthermore, the addition of grafts to the dendrimer were seen to reduce the required tension for membrane rupture and release the genetic material.

The results in this work provide perspective on both the general manner through which dendrimers permeate cellular membranes and how neutral grafts affect dendrimer-membrane interactions. When the optimally designed grafted dendrimers are near the cell membrane at physiological pH, they will not insert themselves into the membrane; however, upon internalization, the drop in pH and corresponding protonation of the tertiary amine groups results in favorable dendrimer-membrane interaction. The insertion of the dendrimer into the bilayer in turn reduces the tension required for the endosomal membrane to rupture which helps to release the internalized material.

- Publications Resulting: One publication.

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