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FINAL REPORT

**Study of Hydrophobic and Ionizable Hydrophilic Copolymers at Polymer/Solid
and
Polymer/Liquid Interfaces**

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Study Goals and Rational

Funds were awarded to resolve the factors that control the stability and integrity of the interfaces between co-polymers consisting of rigid hydrophobic and ionizable hydrophilic blocks at the solid/air and solid/liquid interfaces. The effects of penetration of solvents into these films were then investigated, with the long term goal of designing complex systems for sustainable energy applications.

Joint experimental-computational efforts were set to characterize the interfacial effects on the structure and dynamics of polymers consisting of highly rigid hydrophilic-ionizable and hydrophobic sub-units within one polymeric chain casted into thin films of several molecular dimensions. Focusing on the ultra thin film region we separate out the interfacial effects from bulk characteristics. Specifically, the study sought to: identify the parameters that control the formation of a stable polymer-solid interface. Specifically:

- identify bulk structure and structural changes as a result of interfacial forces;
- characterize the mechanism of spreading and simultaneous interpenetration of small molecules on and into these films;
- characterize the structure of the polymer film as it is solvated;
- resolve interfacial dynamics of the polymers and the solvents.

The study consists of two components, experimental investigations and computational efforts. The experimental component was designed to derive empirical trends that can be used to correlate the set of coupled polymer molecular parameters with the interfacial characteristics of these polymers, and their response to presence of solvents. The computational study was designed to provide molecular insight into the ensemble averages provided by the experimental efforts on multiple length scales from molecular

dimensions, to the nanometer lengths to a macroscopic understanding of solvent interactions with structured polymers. With the ultimate goal of correlating molecular parameters to structure, dynamics and properties of ionic polymers, the first stage of the research began with the study of two systems, one which allowed tailoring the flexibility of the backbone without the presence of ionic groups, but with a potential to sulfonate groups at a later stage, and a polymer whose backbone is rigid and the density of the ionic group can be varied.

The combined experimental and computational studies significantly extended the understanding of polymers at interfaces from model systems to polydispersed copolymers with blocks of varying nature and complexity. This new insight directly affects the design of polymers for sustainable energy applications from batteries and fuel cells to solar energy.

ACHIEVEMENTS

Experimental

The initial premise of the proposal has been that both the bulk and interfacial structure of the polymers on multiple length scales affects the penetration of solvents into complex macromolecular films. With this hypothesis we have investigated how the bulk structure is correlated with transport measurements in nanometer to millimeter thick thin films of rigid ionomers.

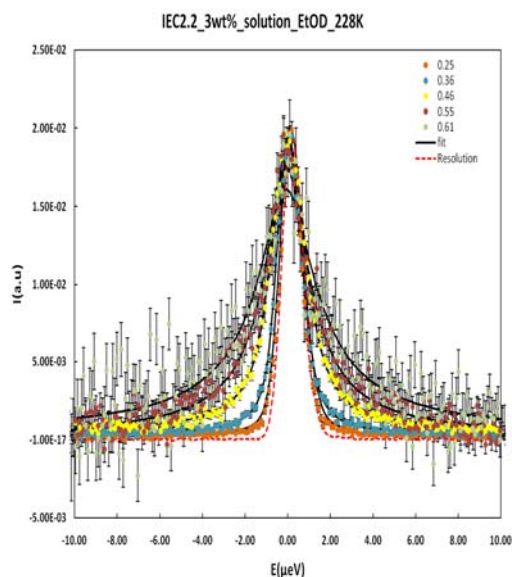
Membranes The bulk structure of rigid ionomers, sulfonated substituted polyphenylene ionomers, (sPP) has been investigated. These polymers were originally developed as an alternative for polymer electrolytic membranes in fuel cells. They consist of a polyphenylene core substituted by aromatic rings with random sulfonation on the substituents. Their rigid backbone is what distinguishes these polymers from common ionomers used in electrochemical applications and affects their conformation and association modes in solution and in thin membranes. Small angle neutron scattering (SANS) studies have shown that these ionomers in their acid form, associate into bundles in dilute organic solutions, whose structure is hardly affected by temperature and only slightly by the degree of sulfonation. Further structural studies including SANS and X-ray scattering of the polymers in the condensed phase have shown that the bundle structure that dominates the solution properties persists in the membranes. When hydrated, water first penetrates in between the domains followed by rearrangement and eventual formation of local bicontinuous structures. This rearrangement is only slightly dependent on temperature and sulfonation level. In comparison with flexible ionomers, no ionic clusters are observed in the dry membranes, and for most membranes bicontinuity propagates over limited regions of the membranes.

Thin Films: Water diffusion into ultrathin sulfonated polyphenylene (sPP) ionomer films was investigated as a function of time, ionic strength and film thickness by neutron reflectometry (NR). The films were characterized by a non-uniform distribution of water.

There is a high water concentration at the air-polymer interface, which decreases in concentration as the silicon-polymer interface is approached. The water diffusion into the film occurs in two stages, in which water first wets the surface and then penetrates into the film. Initial water diffusion into sPP is characterized as Fickian diffusion, which transitioned to an anomalous diffusion with extended exposure to water. Water diffusion was found to be dependent on ionic strength and film thickness.

Thin Films: Methanol The interactions of the polymers with guest molecules have been further investigated following the penetration of methanol into the films. The ionomer films were exposed to saturated deuterated methanol vapor and reflectometry patterns were recorded until equilibrium was reached. The process incorporates two stages where the vapors first wet the surface and then penetrate into the film. Significant swelling takes place as soon as the film is exposed to methanol vapor. Similar to previous studies in water, the onset diffusion is Fickian followed by an anomalous diffusion process. The entire process however is faster than that observed for water.

Dynamic Studies The dynamic of water within sPP has been investigated. An example of backscattering results in a gel phase formed by sPP in deuterium labeled ethanol is shown in Figure 1. The signal arises from the protonated component where dynamics is reflected in broadening of the line with respect to a standard (solid vanadium in this case). The motion observed in this example corresponds to that of the substituted aromatic rings.



The data are analyzed in terms of a stretched exponential with the relaxation time derived by Kohlrausch-Williams-Watt (KWW) $\phi_{KWW}(t) = A \exp[-(t/\tau)^\beta]$ and dynamic parameters are extracted.

Our studies have shown that on the time frame of the measurement, the polymer remains rigid and the water moved along the polymer bundles.

Figure 1: A back scattering neutron intensity at different length scales as indicated by the q values of a three wt% of sPP with sulfonation of 33 mol% at 228K in deuterated ethanol. At this temperature a gel phase is formed.

Interfacial diffusion of the polymer backbone. The mesoscopic dynamics of the polymer backbone is slower than that of the water and is not detectable by inelastic neutron techniques. In order to understand the motion of the polymer we have investigated a model system, polystyrene sulfonate. As a first stage we followed the migration of deuterated polystyrene into protonated layers as shown in Figure 2 with the next step (reflectivity run August 3-8 in Lujan Center, LANL), sulfonated groups will be incorporated into the PS.

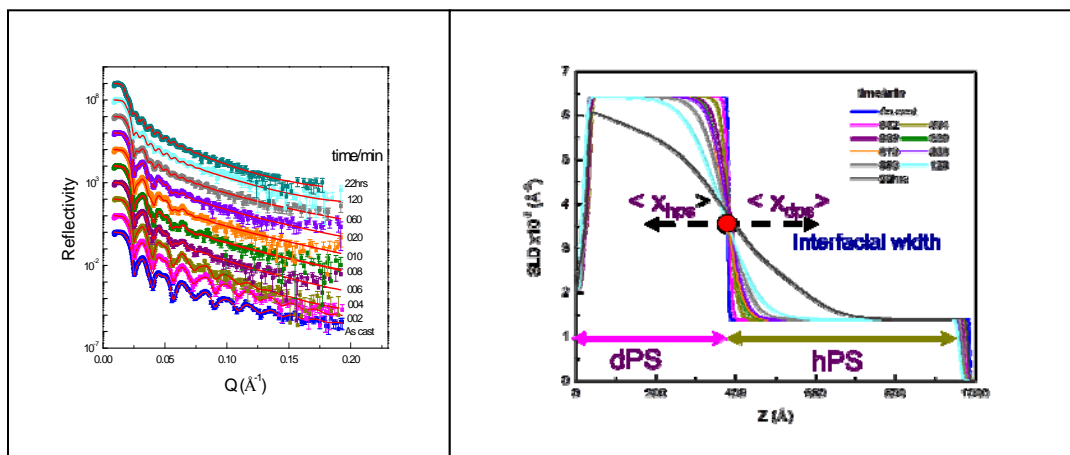


Figure 2. Reflectometry studies of protonated polystyrene Mw170k hPS diffusing into a 140k dPS at 107°C (left). On the right, the polymer profiles derived from the reflectometry studies are shown.

For a first approximation, our measurements followed the results of Russel and co-workers, however with improving reflectometry q range, further details have been revealed, which are currently summarized in a manuscript. Based in these experiments, the sulfonation level of the polymers will be enhanced.

Computational

Computationally the main task has been to build highly segregated polymers and to prove that we can obtain meaningful results over the time and length scales that will allow us to correlate experimental and computational studies. To do so we took two pathways. We first investigated atomistically semifluorinated polymers, who are rigid polymers, as a model system. These polymers have been studied in contact with their own vapor and with other liquids. The second approach taken was to simulate a coarse-grained polymer model and follows its interfacial behavior on a larger length scale. The proof of concept obtained with these model systems is a first towards investigating the ionic polymers of interest on multiple time and length scales. Long term we seek to develop coarse grain models that incorporate the atomistic properties which allowing us to capture a large realistic membrane.

Liquid Vapor Interface The liquid-vapor interfacial properties of semifluorinated linear alkane diblock copolymers of the form $F_3C(CF_2)_{n-1}(CH_2)_{m-1}CH_3$ were studied by fully atomistic molecular dynamics simulations. The chemical composition and the conformation of the molecules at the interface were identified and correlated with the interfacial energies. On the methodology side, two different potentials were compared, OPLS force field of Jorgensen *et al.* and exp-6 force field of Borodin *et al.* developed specifically for this study. Both force fields yield good agreement with available experimental liquid density and surface tension data as well as each other over significant temperature ranges and for a variety of chain lengths and compositions. The interfacial regions of semifluorinated alkanes was found to be rich in fluorinated groups compared

to hydrogenated groups, an effect that decreased with increasing temperature but was independent of the fractional length of the fluorinated segments. The proliferation of fluorine at the surface substantially lowers the surface tension of the diblock copolymers, yielding values near those of perfluorinated alkanes and distinct from those of protonated alkanes of the same chain length.

Liquid-Liquid Interface The liquid-liquid interface between semifluorinated alkane diblock copolymers and a variety of solvents including H₂O, protonated alkanes, and perfluoroalkanes were studied by fully atomistic molecular dynamics simulations. Aqueous interfaces are found to be sharp, with correspondingly large values of the interfacial tension. Due to the reduced hydrophobicity of the protonated block compared to the fluorinated block, these regions showed enhancement in hydrogen over fluorine at the interface. Water dipoles in the interfacial region were found to be oriented nearly parallel to the liquid-liquid interface. A number of protonated alkanes and perfluoroalkanes were found to be mutually miscible with the semifluorinated diblocks. For these solvents, interdiffusion follows the expected Fickian behavior. The concentration dependent diffusivities were determined for a number of systems.

Coarse Grained Systems. In order to study large enough systems to be compared with scattering experiments, we initiated coarse grained studies of interfacial phenomena including wetting and interpenetration. In parallel to the experimental work, computational studies were carried to provide further understanding of the effects discussed above. Two issues were investigated: a- the characteristics of wetting on responsive surfaces; b-dynamics at the polymer-polymer interface.

Spreading At a Responsive Interface.

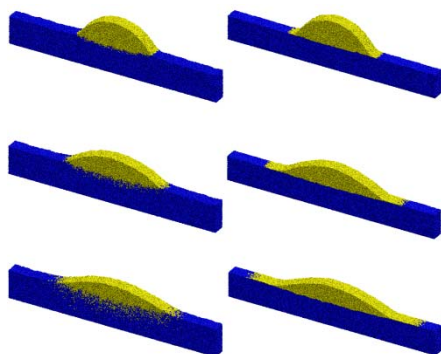


Figure 3 Droplet of 10 beads (presented in yellow) spreading on liquid polymer (presented in blue) films at $t = 4000, 20000, 80000\tau$ (top to bottom) (left) and glassy polymer film at $t = 4000, 20000, 40000\tau$ (right)

In contrast to solid surfaces, spreading of liquids on top of polymers is accompanied by a process of penetration that changes the polymer itself and affects the spreading. This issue becomes even more important when the polymers form non-homogeneous interfaces. We found that the degree of interpenetration and amount of damping from the film depends on the viscosity of the film and the relative interaction of the droplet and film. Shown in Figure 3 is a snapshot for a liquid drop on a low (left) and high (right) viscosity film. For low viscosity liquid films, the interpenetration of the droplet follows a $t^{1/2}$ Fickian power law and the droplet spreads without a precursor foot. For very viscous films a precursor foot spreads ahead of the film, and the droplet does not penetrate the film.

An important characteristic of some ionic polymers is that of self healing, where spontaneous rearrangements take place to recover from either mechanical damage or changes in structure that take place following exposure to solvents. In this process polymeric interfaces merge to form continuous films. Merging

of polymeric interfaces was studied by coarse grain molecular dynamics simulations and formation of entanglements across the interface was followed using primitive path analysis. Shown in Figure 4 is a snapshot of the interface between two interpenetrating entangled polymers and a primitive path analysis of the entanglements between the two films after a specified time. This is the first time where the onset of formation of entanglements has been observed.

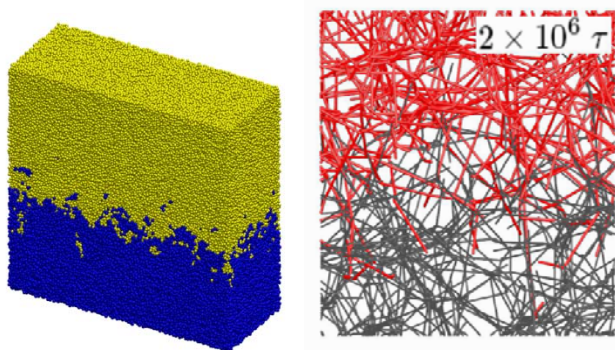


Figure 4: Left: A snapshot of the interfacial region for two entangled liquid polymer films of length $N=500$ after interpenetrating for $2 \times 10^6 \tau$ and a primitive path representation of the same interface.

Synergy

In our efforts to determine interfacial behaviour of ionic polymers, we have investigated several different systems to provide a proof of concept and to demonstrate that we can a) resolve invaluable information from different neutron techniques when data are fully analyzed; b) demonstrate that we can simulate large enough systems to be able to compare with experimental scattering work.

The research has been carried out simultaneously at Clemson and Sandia and at several neutron facilities. Dr. Lilin He graduated and is a beam line scientist in Oak Ridge National Laboratory. Dr. Flint Pierce is at Sandia National Laboratories.

Mr. Umesh Streshta, Mr. Thusitha Etampawalla and Mr. Dipak Aryal have been working on the project. The PI and Gary Grest are co-advising the students. Monthly visits of both scientists ensure ongoing communication take place. All personal are involved in both neutron scattering and simulations.

Information Dissemination

Publications

1. Pierce, F.; Tsige, M.; Borodin, O.; Perahia, D.; Grest, G. S., **Interfacial Properties of Semifluorinated Alkanes**, J. Chem. Phys. (2008) 128, 214903-1 – 214903-14.
2. Pierce, F.; Tsige, M.; Perahia, D.; Grest, G. S., **Liquid-Liquid Interfaces of Semifluorinated Alkane Diblock Copolymers with Water, Alkanes, and Perfluorinated Alkanes**, J. Phys. Chem. B (2008) 112, 16012-16120.
3. Pierce, F.; Perahia, D.; Grest, G. S., **Interdiffusion of Short Chain Oligomers into an Entangled Polymer Film**, Macromolecules (2009) 42, 7969-7973.

4. Pierce, F.; Perahia, D.; Grest, G. S., **Spreading of Liquid Droplets on Permeable Polymeric Surfaces**, EPL (2009) 86, 64004/1-64004/5.
5. He, Lilin; Smith, Hillary L.; Majewski, Jaroslaw; Fujimoto, Cy H.; Cornelius, Christopher J.; Perahia, Dvora, **Interfacial Effects on Water Penetration into Ultrathin Ionomer Films: An in Situ Study Using Neutron Reflectometry**, Macromolecules (2009) 42, 5745-5751.
6. He, Lilin; Fujimoto, Cy H.; Cornelius, Chris J.; Perahia, Dvora, **From Solutions to Membranes: Structure Studies of Sulfonated Polyphenylene Ionomers**, Macromolecules (2009) 42, 7084-7090.
7. Pierce, F.; Perahia, D.; Grest, G. S., **Interfacial effects of nanometer fluorinated segments on energy controlled responsive polymeric films: molecular dynamic simulations**, Polymer Preprints (American Chemical Society, Division of Polymer Chemistry) (2009) 50, 150-151.
8. Pierce, F.; Perahia, D.; Grest, G. S., **Dynamics of Polymers Across an Interface**, EPL (2011) 95, 46001.
9. Anyprya Agrawal, Dipak Aryle, Gary Grest, Dvora Perahia **Interfacial Response of Semifluorinated Multi-block co-Polymers** Invited to: *Handbook of Fluorinated Materials* (2014).
10. He, L.; Cornelius, C. J.; Perahia, D., **Water Dynamics in Highly Rigid Ionic Membrane: NMR and IR Study**, J Polymer Science Part B: Polymer Physics, *submitted*.

Presentations

1. Thusitha Etampawala, Dilru Ratnaweera, Naresh Osti, Umesh Shrestha, Dvora Perahia **Interfacial Effects on Pentablock Ionomer Thin Films** APS March Meeting, March 21–25, 2011; Dallas, Texas.
2. Dipak Aryal, Dvora Perahia, Gary S. Grest **Conformation of Randomly Sulfonated Pentablock Ionomers in Dilute Solution: Molecular Dynamic Simulation Study**, APS March Meeting, March 21–25, 2011; Dallas, Texas.
3. Naresh Osti, Thusitha Etampawala, Umesh Shrestha, Christopher Cornelius, Dvora Perahia **Dynamics of water in sulfonated poly(phenylene) membranes**, APS March Meeting, March 21–25, 2011; Dallas, Texas.
4. Thusitha Etampawala, Dilru Ratnaweera, Umesh Shrestha, Dvora Perahia, Christopher Cornelius, Jaroslaw Majewski, **Interdiffusion of long alcohols into thin ionomer films; In situ Neutron Reflectivity study**, APS March Meeting, March 15–19, 2010; Portland, Oregon.
5. Gary S. Grest, Flint Pierce, Dvora Perahia, **Molecular dynamics simulations of responsive semi-fluorinated interfaces**, 240th ACS National Meeting, August 22–26, 2010, Boston, Massachusetts.

6. Gary S. Grest, **Interdiffusion and Self-Healing of Entangled Polymer Melts** APS March Meeting, March 15–19, 2010; Portland, Oregon (invited).
7. Flint Pierce, **Molecular Dynamics Simulations of Responsive Semi-Fluorinated Interfaces**, APS March Meeting, March 15–19, 2010; Portland, Oregon (invited).
8. Umesh M. Shrestha, Stephen J. Clarson, Jim F. Browning, and Dvora Perahia **Semi-fluorinated Polymers Confined at the Solid-Air Interface**, APS March 16–20, 2009; Pittsburgh, Pennsylvania.
9. Thusitha Etampawala, Christopher J. Cornelius, Jaroslaw Majewski, Lilin He, and Dvora Perahia **In Situ Neutron Reflectivity Study of Long Chain Alcohols Diffusion Into Thin Ionomer Films**, APS March 16–20, 2009; Pittsburgh, Pennsylvania.
10. Flint Pierce, Dvora Perahia, and Gary S. Grest, **Spreading of Droplets on Viscous Polymer Liquids**, APS March 16–20, 2009; Pittsburgh, Pennsylvania.
11. Thusitha, N. Etampawala, Lilin He, Christopher J. Cornelius, Jaroslaw Majewski, and Dvora Perahia, **Long chain alcohol penetration into ultra-thin ionomer films: An in situ kinetic study using Neutron Reflectivity**, International Neutron Scattering Meeting, 2009, Oak Ridge, Tennessee.
12. Umesh Shrestha, Stephen Clarson, Dvora Perahia, **Scattering Neutron Reflectivity Study of Fluorine Containing Diblock Copolymers**, International Neutron Scattering Meeting, 2009, Oak Ridge, Tennessee.
13. Lilin He, Thusitha N. Etampawalla, Jaroslaw Majewski, Christopher J. Cornelius and Dvora Perahia., **Methanol Diffusion into Thin Ionomer Films: An in situ Study Using Neutron Reflectometry**, APS March Meeting, March 10–14, 2008; New Orleans, Louisiana.
14. Flint Pierce, Dvora Perahia, Mesfin Tsige, Oleg Borodin, and Gary S. Grest **Interfacial Properties of Semi fluorinated Alkane Diblock Copolymers**, APS March Meeting, March 10–14, 2008; New Orleans, Louisiana.
15. Flint Pierce, Dvora Perahia, Mesfin Tsige, Oleg Borodin, and Gary S. Grest **Interfacial Properties of Semifluorinated Alkane Diblock Copolymers**, CINT User Meeting January 9, 2008.

Personal

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