FINAL REPORT

DOE award # DE-SC0003912

Name and address of recipient organization: University of Colorado, Boulder CO 80309

Project Title: Theory and simulations of Tailored Assembly in Rod Coil Polymer Nanocomposites

PI name: Arthi Jayaraman,

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(Current Title and Position) Associate Professor, University of Delaware, Newark

Dates covered: 04/15/2010 – 04/15/2015

Date of the final report (January 20th 2016)

Executive Summary

This DoE supported early career project was aimed at developing computational models, theory and simulation methods that would be then be used to predict assembly and morphology in polymer nanocomposites. In particular, the focus was on composites in active layers of devices, containing conducting polymers that act as electron donors and nanoscale additives that act as electron acceptors. During the course this work, we developed the first of its kind molecular models to represent conducting polymers enabling simulations at the experimentally relevant length and time scales. By comparison with experimentally observed morphologies we validated these models. Furthermore, using these models and molecular dynamics simulations on graphical processing units (GPUs) we predicted the molecular level design features in polymers and additive that lead to morphologies with optimal features for charge carrier behavior in solar cells. Additionally, we also predicted computationally new design rules for better dispersion of additives in polymers that have been confirmed through experiments. Achieving dispersion in polymer nanocomposites is valuable to achieve controlled macroscopic properties of the composite. The results obtained during the course of this DOE funded project enables optimal design of higher efficiency organic electronic and photovoltaic devices and improve every day life with engineering of these higher efficiency devices.

A brief description of accomplishments and the products we created during the course of this DOE funded project.

We list below the products in the form of **peer reviewed research articles** as well as accomplishments in the form of **awards/honors received by PI Jayaraman and graduate student Hilary Marsh** for this work. The title and full citation, sections of the abstract and the table of contents image for that paper are presented below. Please note that the abstract and images are obtained from the journal website.

1. *E. Jankowski[#], H. S. Marsh[#], A. Jayaraman*, Computationally linking molecular features of conjugated polymers and fullerene derivatives to bulk heterojunction morphology* ***Macromolecules*** *2013 ([#] equal contribution) 46 (14) 5775-5785 (2013)* (This was one of 20 most downloaded articles from Macromolecules in July 2013)

In this paper we present a high-throughput coarse-grained simulation study that links molecular-level design parameters to features in the assembled morphology in neat polymers and donor–acceptor blends. These models reproduce neat polymer morphologies observed in experiments, such as lamellae, hexagonally packed cylinders, and acceptor intercalation among donor side chains. Furthermore, for blends of conjugated polymers and fullerene derivatives, this study shows how conjugated polymer architecture and acceptor miscibility can be tailored to obtain new blend morphologies, which have features that are known to be optimal for higher efficiency solar cells.

2. *H. S. Marsh, E. Jankowski,* ***A. Jayaraman****, Controlling the morphology of model conjugated thiophene oligomers through alkyl side chain length, placement and interactions* ***Macromolecules*** *(2014)*
   http://pubs.acs.org/doi/abs/10.1021/ma5000267In this paper we have performed coarse-grained molecular dynamics simulations of thiophene-based conjugated oligomers to elucidate how the oligomer architecture, specifically the orientation and density of alkyl side chains extending from the thiophene backbones, impacts the order-disorder temperatures and the various ordered morphologies that the oligomers form.

3. *L. Zhang, F. Liu, Y. Diao, H. S. Marsh, N. Collela,* ***A. Jayaraman****, T. P. Russell, S. C. Mannsfeld*, A. Briseno*, The good host: formation of discrete fullerene "autobahnen" in well-ordered BTTT Oligomers J.Am. Chem. Soc (2015)* http://pubs.acs.org/doi/abs/10.1021/ja510976n
   In this paper using the models that we developed during the course of this DOE project we simulated and predicted the structure of neat BTTT oligomers (monomers and dimers in specific) and blends of BTTT oligomers with PBCM. We found a remarkable agreement between our computationally predicted structures and experimental observation of fullerene derivative (PCBM) aligning in BTTT phase.

4. *T. Martin, A. Jayaraman*, Polydisperse homopolymer grafts stabilize dispersions of nanoparticles in a chemically identical homopolymer matrix: an integrated theory and simulation study,* ***Soft Matter*** *9 (29), 6876 – 6889* ***(****2013) (This article was published in the special issue on '****Emerging Investigators in Soft Matter'*** *)*

This paper presents a computational study of the effect of polydispersity in grafted polymers on the effective interactions between polymer grafted nanoparticles in a polymer matrix, when graft and matrix polymers are chemically identical.

5. *T. Martin, A. Jayaraman*, Identifying the ideal characteristics of a polydisperse polymer graft length distribution for maximizing dispersion of polymer grafted nanoparticles in a polymer matrix* ***Macromolecules*** *46 (22), pp 9144–9150 (2013)*

We investigate, using theory and simulations, the role of the short and long grafted chains in polydisperse polymer grafted nanoparticles in stabilizing particle dispersion in a chemically similar polymer matrix in the presence of particle–particle attractions.

6. *V. Ganesan* and A. Jayaraman*, Theory and simulation studies of effective interactions, phase behavior and morphology in polymer nanocomposites, Invited peer-reviewed review article to* ***Soft Matter****,* ***10****, 13-38 (2014)*

In this article we review recent theory and simulation studies, presenting briefly the methodological developments underlying PRISM theories, density functional theory, self-consistent field theory approaches, and atomistic and coarse-grained molecular simulations. We first discuss the studies on polymer nanocomposites with bare or un-functionalized nanoparticles as additives, followed by a review of recent work on composites containing polymer grafted or functionalized nanoparticles as additives. We conclude each section with a brief outlook on some potential future directions.

7. *A. Jayaraman*, Polymer Grafted Nanoparticles: Effect of Chemical and Physical Heterogeneity in Polymer Functionalization on Particle Assembly and Dispersion, Invited Peer-reviewed Feature Article for special issue* ***highlighting innovative young polymer researchers*** *in* ***Journal of Polymer Science B: Polymer Physics*** *51(7), 524–534 (2013)*

In this feature article, we present our recent theory and simulation studies of polymer grafted nanoparticles with chemical and physical heterogeneity in grafts to calculate the effective interactions and morphology as a function of chemistry, molecular weights, grafting densities, and so forth.

8. *C. E. Estridge,* ***A. Jayaraman****, Effect of homopolymer matrix on diblock copolymer grafted particle conformation and potential of mean force: a molecular simulation study, J Polymer Science B: Polymer Physics (2015) 53, 76-88*
   Selected for Journal Cover Art (see figure on left)
   http://onlinelibrary.wiley.com/doi/10.1002/polb.23637/full

In this paper we have conducted extensive coarse-grained molecular simulations to show how one can obtain patchy particles using block copolymer grafted particles placed in a homopolymer matrix. We have shown that AB diblock copolymer grafted particles, where the copolymers are grafted using A block, when placed in A homopolymer matrix adopt patchy conformations. On the other hand in a B homopolymer matrix the particle adopts a core-corona conformation. We have also conducted biased MD simulations to calculate potential of mean force between particles to show we can design the diblock copolymer graft to tune attractions and positions of attractions and repulsions between particles in the medium. This work was also highlighted on the cover of this Journal.

9. *B. Lin, T. Martin,* ***A. Jayaraman****, Decreasing Polymer Flexibility Improves Wetting and Dispersion of Polymer Grafted Particles in a Chemically Identical Polymer Matrix* ***ACS Macroletters****, (2014) 3, pp 628–632 http://pubs.acs.org/doi/abs/10.1021/mz500274w*

In this paper, using theory and simulation the flexibility of polymer grafts is explored and its effect on dispersion of particles is studied. We have predicted that decreased flexibility of grafts (e.g. in conjugated polymers where the persistence length is high) leads to improved particle dispersion in a chemically identical polymer matrix. In the context of organic electronics if electron acceptor materials are functionalized with the electron donor conjugated polymers we will be able to disperse them in chemically identical conjugated polymer matrix more easily than non-conjugated polymers. This provides a new route for morphological control.

10. *T. Martin, **A. Jayaraman***, Effect of Matrix Bidispersity on the Morphology of Polymer Grafted Nanoparticle filled Polymer Nanocomposites' **J. Polymer Science B: Polymer Physics** (2014) (Special Issue on "Hairy Nanoparticles") 52, 1661-1668*

In this paper we describe using coarse-grained molecular simulations that polydispersity in matrix polymers does not improve polymer grafted particle dispersion in a polymer matrix. This is valuable to know as we have previously predicted (and have experimentally been proved right) that polydispersity in graft polymers does indeed improve particle dispersion in monodisperse polymer matrix. This study notes that a similar beneficial effect is not obtained if the polydispersity was incorporated in the matrix.

11. *C. Estridge, **A. Jayaraman*,** Assembly of diblock copolymer functionalized spherical nanoparticles as a function of copolymer composition. **J. Chem Phys** (2014) 140 (14) 144905 http://scitation.aip.org/content/aip/journal/jcp/140/14/10.1063/1.4870592*

In this work, we use coarse-grained molecular dynamics simulations to study spherical nanoparticles functionalized with AB diblock copolymer chains at low grafting density, to obtain a design library linking copolymer composition, monomer-monomer interaction strengths, graft lengths, particle sizes, and monomer solvent-philicity to the two stages of nanoparticle assembly: the initial formation of patches within the copolymer-grafted particles from attractive monomers aggregating, and then the (equilibrium) assembled cluster formation.

12. *C. E. Estridge, A. Jayaraman, Diblock copolymer grafted particles as compatibilizers for immiscible homopolymer blends* **ACS Macroletters** (2015) 4 (2), pp 155 *pubs.acs.org/doi/abs/10.1021/mz500793e*

In this paper using coarse-grained molecular simulations we study AB diblock copolymer grafted particles (DBCGPs) as compatibilizers in an immiscible blend of A and B homopolymers. We found that the fraction of the A block in the graft, f_A, tunes the location of the DBCGPs within the blend. When f_A=0.25, the DBCGPs preferentially localize in the B domain of the blend, and when f_A= 0.5 and 0.75, the DBCGPs localize at/near the interface of the A and B domains, adopting conformations that segregate the A and B segments of the grafts into chemically identical domains of the blend. The desorption energy to leave the interface and the drop in interfacial tension is larger for the DBCGP than ungrafted diblock copolymers, commonly used as compatibilizers. Additionally, the comparable reduction in interfacial tension of DBCGPs as Janus-homopolymer grafted particles, along with the easier synthesis routes of DBCGP, makes DBCGP an attractive alternative class of compatibilizers for polymer blends.

13. *T. B. Martin#, K. I. Mongocopai#, R. Ashkar, P. Butler, R. Krishnamoorti*, A. Jayaraman* 'Wetting-Dewetting and Dispersion-Aggregation Transitions are Distinct in Mixtures of Polymer Grafted Nanoparticles and a Chemically Dissimilar Polymer Matrix' **J. Am. Chem. Soc.** 2015, 137 (33), pp 10624–10631 http://pubs.acs.org/doi/abs/10.1021/jacs.5b05291*

In this paper we present simulations and experiments conducted on mixtures containing polymer grafted nanoparticles in a chemically distinct polymer matrix, where the graft and matrix polymers exhibit attractive enthalpic interactions at low temperatures that become progressively repulsive as temperature is increased. Both coarse-grained molecular dynamics simulations, and X-ray scattering and neutron scattering experiments with deuterated polystyrene (dPS) grafted silica and poly(vinyl methyl ether) PVME matrix show that the sharp phase transition from (mixed) dispersed to (demixed) aggregated morphologies due to the increasingly repulsive effective interactions between the blend components is distinct from the continuous wetting–dewetting transition. Strikingly, this is unlike the extensively studied chemically identical graft–matrix composites, where the two transitions have been

considered to be synonymous, and is also unlike the free (ungrafted) blends of the same graft and matrix homopolymers, where the wetting–dewetting is a sharp transition coinciding with the macrophase separation.

Recognition Received for this DOE supported work

Awards/Honors for PI Arthi Jayaraman

- ACS Polymeric Materials Science and Engineering (PMSE) Young Investigator 2014
- University of Colorado Provost Faculty Achievement Award 2013
- AIChE Computational Molecular Science and Engineering Forum (COMSEF) Young Investigator Award 2013
- PI Jayaraman has given 30+ invited talks on this DOE funded work at various national meetings and university seminars. See her CV on http://www.che.udel.edu/pdf/facultycv/33673cv.pdf

Awards/Honors for graduate students involved in this DOE supported work

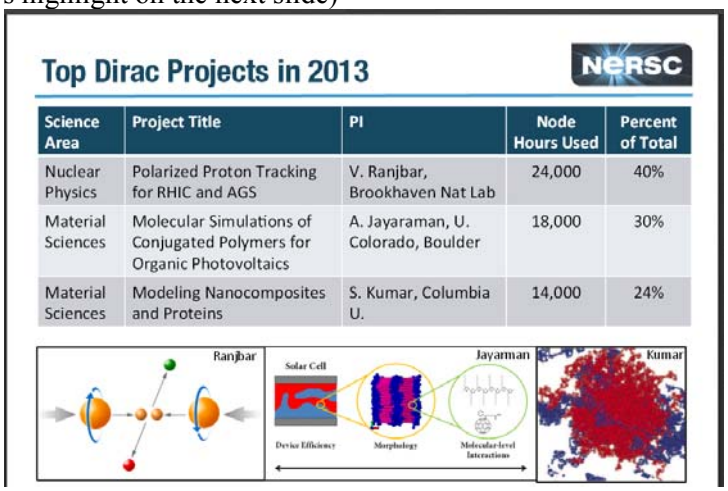
Honors for Hilary Marsh

Excitonic Photovoltacis (XPV) Best Research Poster award 2014
MRS Fall meeting 2014 Best Oral Research Presentation (Symposium Q: Organic semiconducting materials)

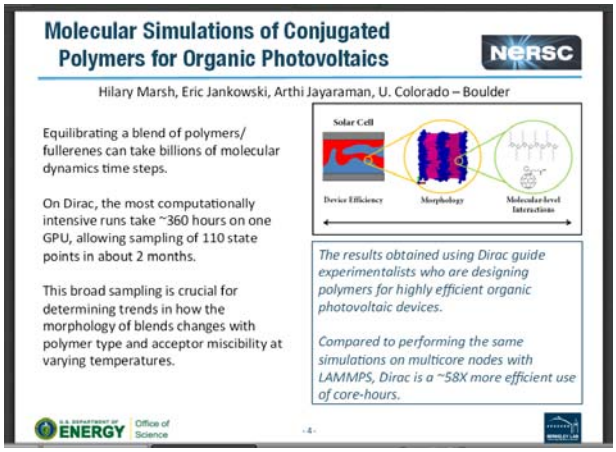
Honors for Mr. Tyler Martin

Selected Finalist of "Excellence in Polymer Graduate Research" AICHE Annual Meeting 2015
Selected Finalist in "Padden symposium for Excellence in Graduate Research" APS March Meeting 2016

News Highlight on NERSC (DOE funded supercomputing resources used for this work)
Our supercomputing use for this DOE supported research (Topic 1) was highlighted in NERSC website for being one of the top three users on Dirac (GPU resources) on NERSC.
(See images from news highlight on the next slide)



Images from the news highlight on http://www.nersc.gov/assets/pubs_presos/Diracscience.pdf



A list of people working on the project -graduate students, postdocs, visitors, technicians, etc. Indicate for each whether receiving full or partial support.

a) Prof. Arthi Jayaraman (PI) – 1 summer month salary in 2010-2014
b) Ms. Hilary Marsh (graduate student) – fully supported from 01/2011- 12/2012, and then 50% supported from 01/2013 to 04/2015 (end of the project)
c) Mr. Tyler Martin (graduate student) – partial support from 01/2013 – 05/2013
d) Dr. Eric Jankowski (postdoc) – partially supported from 01/2013 – 03/2014
e) Dr. Dongsheng Zhang (postdoc) fully supported from 06/2010-09/2011
f) Mr. Charles Starbird (graduate student) – fully supported from 01/2011-06/2012
g) Ms. Carla Estridge (graduate student) – partial support from 01/2013-04/2015 (end of the project)

Details of a new Molecular Model Developed During the Course of This Project

E. Jankowski[#], H. S. Marsh[#], A. Jayaraman, Computationally linking molecular features of conjugated polymers and fullerene derivatives to bulk heterojunction morphology* ***Macromolecules*** *2013 ([#] equal contribution) 46 (14) 5775-5785 (2013)* (This was one of 20 most downloaded articles from Macromolecules in July 2013)

In this paper we presented a new coarse-grained model and a high-throughput graphical processing unit (GPU) based simulation study that links molecular-level design parameters to features in the assembled morphology in neat polymers and donor–acceptor blends.

The details of the new model – physical and chemical interactions are presented in the main manuscript as well as the supplementary information.

http://pubs.acs.org/doi/suppl/10.1021/ma400724e

We show that these models reproduce neat polymer morphologies observed in experiments, such as lamellae, hexagonally packed cylinders, and acceptor intercalation among donor side chains. This serves as validation of these new coarse-grained models.