UNIVERSITY OF MASSACHUSETTS AMHERST

Center for UMass Industry Research on Polymers (CUMIRP)

Research Cluster F: Fire-Safe Polymers and Polymer Composites

FINAL REPORT
August 2009

Todd Emrick
Principle Investigator

Federal Aviation Administration
Grant No. 99-G-035

Final report to the Federal Aviation Administration for grant # 99-G-035, 08/2006 to 08/2009

P.I. Todd Emrick
Polymer Science & Engineering Department
University of Massachusetts
Amherst, MA 01003

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This report is intended to serve as a final summary report for activities sponsored by the Federal Aviation Administration award at the University of Massachusetts Amherst under grant # 99-G-035. This FAA grant supported efforts associated with the synthesis, properties, and theoretical treatment of polymer materials that promote advances in the science and technology of low flammability materials. The fundamental and technological discoveries made during the course of the grant period were substantial, as indicated in the accompanying pages listing publications and patent applications. This report provides a broad overview of the activities under FAA sponsorship during the grant period; more specific details of experiments and outcome can be found in the detailed reports submitted to the FAA for each reporting period during the course of the grant.

The FAA award to UMass Amherst was central to efforts at UMass in research on polymer flammability and the generation, characterization, and theoretical understanding of low flammability polymer materials. The FAA award was the core of research on this topic, around which developed a consortium of sponsored research from the U.S. Army and several corporate sponsors. This collection of research activity was organized by the Center for UMass-Industry Research on Polymers (CUMIRP), a long-standing organization in the Polymer Science & Engineering Department at UMass which provides a connection between academic research and interest in the commercial viability of the research. The polymer Flammability "cluster" of research, referred to as "Cluster F", met twice yearly, at which point the sponsored research was presented to participants from the sponsoring organizations. It is from these meetings that the semi-annual research presentations, submitted to the FAA, were generated.

During the course of the FAA funded project on anti-flammable polymer materials (2006-2009), UMass Amherst researchers were engaged in the synthesis and characterization of novel anti-flammable polymers, as well as theoretical and molecular modeling aspects that improve the fundamental understanding of materials flammability. FAA support was responsible for the development of significant expertise among graduate and postdoctoral researchers at UMass, providing the foundation for a research program which also enabled a private sector consortium operation to augment the effort. The productivity of polymer flammability researchers at UMass during this period was substantial, including 8 published manuscripts, 3 patent applications, and the placement of some of our best graduate students and postdoctoral associates into top-notch corporate and government laboratories (including for example the FAA, NIST, Kodak, Shocking Technologies (San Jose, CA) the Korean Institute of Science and Technology (KIST), and ATK Thiokol in Utah.

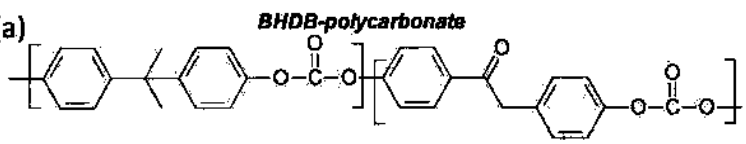
FAA-supported research at UMass Amherst in the area of anti-flammable polymer synthesis, characterization, and modeling/theory was innovative and productive. Syntheses pioneered by **Emrick** on deoxybenzoin-containing polymers developed rapidly from their inception (also during an FAA-sponsored project), producing anti-flammable aromatic polyesters, polyphosphonates, poly(ester-phosphonate) copolymers, polycarbonates, and epoxy polymers. Thermal and mechanical characterization of these materials by **Farris** and **Lesser**

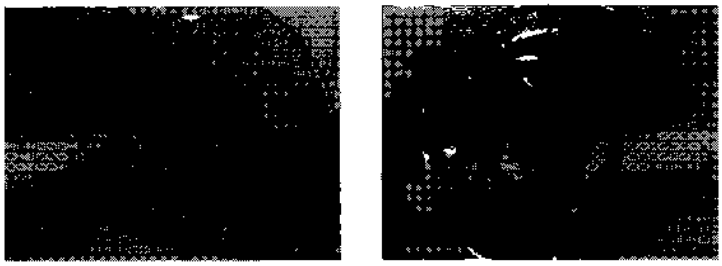
confirmed their predicted ultra-low flammability. Publications in the top-rated polymer journals *Macromolecules* and the *Journal of Polymer Science A: Polymer Chemistry,* describe the synthesis and properties of these new materials. Publication of this research in these high-quality academic journals is most noteworthy given the specialty nature of the polymer flammability topic, and the large and diverse polymer readership of these journals. The popular press became engaged actively in our development of ultra-low flammability polymers, including a *Materials World* feature in 2007.

Our choice several years ago to focus on deoxybenzoin-based polymers for ultra-low flammability was based on a degradation mechanism that suggested deoxybenzoin-based polymers might undergo thermal degradation and char in similar fashion to that of bis-phenol C (BPC). BPC-based polymers, which exhibit appreciable char yields that contribute to its exceptionally low flammability, are chlorine-rich and thus problematic from an environmental standpoint. The halogen-free deoxybenzoin-containing polymers have exhibit impressively low flammability, competitive with that of BPC-polymers, and bis-hydroxydeoxybenzoin (BHDB) is amenable to step-growth polymerization chemistry as a 'drop-in' replacement for BPC or bis-phenol A (BPA). The comparative polymer chemistry and properties of BPA, BPC, and BHDB, placed in the broader scope of polymer materials flammability, has been reviewed recently. In short, it is apparent that BHDB provides facile entry into aromatic polyesters, polyphosphonates, and poly(ester-phosphonate) copolymers with molecular weights ranging from 10,000 g/mole to over 100,000 g/mole. These polymers exhibit heat release capacity (HRC) values, as measured by pyrolysis combustion flow calorimetry, that place them in the ultra-low flammability category.

The physical, mechanical, and thermal/flammability properties of deoxybenzoin-containing polymers were analyzed, and the step-growth polymerizations scaled up to the 50 gram level. Polymerization on this scale provided sufficient material for processing, characterization, and flammability tests performed at the FAA. By all indicators, deoxybenzoin-based condensation polymers can be considered as a most promising class of anti-flammable high-performance polymers with potential societal impact for improving the safety of plastics. Exemplary cases are shown in **Figure 1**, for (a) comparative properties of BHDB- and BPC-based polycarbonate; and (b) results of a UL-94 flammability test performed at the FAA on deoxybenzoin-based aromatic polyesters, in which the high char yield of these polymers led to an excellent performance and an assignment of the lowest flammability 5VA rating.

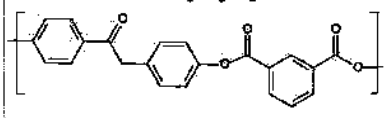
(a) ***BHDB-polycarbonate***

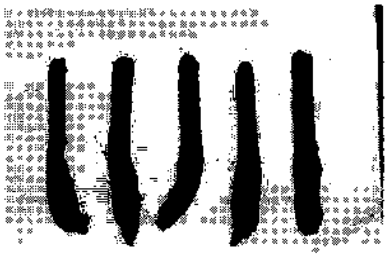




Properties	**BPA-PC**	**BPA-*co*-BHDB-PC (~1:1)**
Morphology	Amorphous	Amorphous
T_g (°C)	145	132
Tensile modulus (GPa)	1.87	1.80
Tensile strength at yield (MPa)	53	50
Elongation at break (%)	7.8	4.6
Char yield (%)	21	27
HR Capacity (J/g-K)	**390**	**138**

(b) ***BHDB-polyarylate***





5VA flammability rating achieved in tests conducted at FAA;

Predominant charring observed

Figure 1. (a) Comparative properties of BPA polycarbonate with a BPA/BHDB random polycarbonate copolymer, demonstrating the higher char yield and lower heat release capacity inherent to the BHDB-containing polymers; (b) results of a flammability test conducted at the FAA on a BHDB-containing aromatic polyesters (BHDB-polyarylate) sample, showing the substantial charring that occurs upon burning these materials.

While we have developed a research platform with deoxybenzoin as the key monomer unit, there remain many unexplored aspects of deoxybenzoin that, if pursued, have excellent potential for impact. Epoxy polymers, polycarbonates, and polyurethanes are prominent among these, as are "high performance" aromatic polycondensation structures. Moving forward, we plan to continuing engaging in the development and discovery of the most promising structures prepared to this point, based on deoxybenzoin. Moreover, we will initiate new projects on nanocomposites of deoxybeznoin-based structures, as well as electrospun fibers and nanotube-polymer composites.

DEPARTMENT OF CHEMICAL ENGINEERING
University of Massachusetts Amherst

PhD Dissertation Defense

Thursday, March 12, 2009
10 AM – Kellogg Conference Room, Elab II

"DEVELOPING REACTIVE MOLECULAR DYNAMICS
FOR UNDERSTANDING POLYMER CHEMICAL KINETICS"

Kenneth D Smith

Directed by: Professor Phillip R Westmoreland

ABSTRACT

One of the challenges in understanding polymer flammability is the lack of information about microscopic events that lead to macroscopically observed species, and Reactive Molecular Dynamics is a promising approach to obtain this crucially needed information. The development of a predictive method for condensed-phase reaction kinetics can provide significant insight into polymer flammability, thus helping guide future synthesis of fire-resistant polymers. Through this dissertation, a new reactive forcefield, RMDff, and Reactive Molecular Dynamics program, RxnMD, have been developed and used to simulate such material chemistry.

It is necessary to have accurate description of chemical kinetics to describe quantitative chemical kinetics. Typical equilibrium forcefields are inadequate for describing chemical reactions due to the inability to represent bonding transformations. This issue was resolved by developing a new method, RMDff that allows standard equilibrium forcefields to describe reactive transitions. The chemical reactions are described by employing switching functions that permit smooth transitions between the reactant and product descriptions available from traditional forcefields. Because all of the chemical motions are described, a complete potential energy surface is obtained for the course of the reaction. Descriptions of scission, addition/beta-scission, and abstraction reactions were developed for hydrocarbon species. Reactive potentials were developed using a representative reaction involving small molecules. It is shown that the overall geometric and energetic changes are transferable to larger and substituted molecules. The main source of error found in RMDff resulted from errors within the equilibrium forcefield descriptions.

In order to simulate the chemical kinetics, it was necessary to create a molecular dynamics program that could implement the reactions from RMDff. RxnMD was developed as a new C++-based Reactive Molecular Dynamics code to simulate the dynamics using RMDff. Polymer kinetics were predicted for high-density polyethylene and used to test the method and code. Conformational changes and polymer length in the initial polyethylene molecules did not significantly alter the backbone decomposition kinetics. The results also revealed that the backbone carbon-carbon bonds could break with an activation energy approximately 100 kJ/mol below the carbon-carbon bond dissociation energy. This decrease was believed to occur from intramolecular polymer stress, which is relieved via backbone scission. Such stress was also observed to increase the beta-scission reaction rate at high temperatures, apparently because the scission reaction alone is not always sufficient to remove the energy associated with the polymer stress concentrated near the scission location. Finally, the RMD method was also shown to be transferable and applicable in describing the decomposition of novel fire-resistant polymers.

The public is cordially invited to attend. Refreshments will be served.

Publication Citations

1. **"Deoxybenzoin-based Epoxy Resins"** Ryu, B-Y; Moon, S.; Kosif, I.; Ranganathan, T.; Farris, R.J.; Emrick, T. *Polymer*, 2009, 50, 767-774.

2. **"Flame Resistant Electrospun Polymer Nanofibers from Deoxybenzoin-based Polymers"** Moon, S.; Ku, B.; Emrick, T.; Coughlin, E.B.; Farris, R.J. *Journal of Applied Polymer Science*, 2009, Vol. 111, Issue 1, 301-307.

3. **"Thermal Degradation of Deoxybenzoin Polymers Studied by Pyrolysis-gas Chromatography/mass Spectrometry"** Ranganathan, T.; Beaulieu, M.; Zilberman, J.; Smith, K.; Westmoreland, P.; Farris, R.J.; Coughlin, E.B.; Emrick, T. *Polymer Degradation and Stability*, 2008, Vol. 93, Issue 6, 1059-1066.

4. **"RMDff: A Smoothly Transitioning, Forcefield-Based Representation of Kinetics for Reactive Molecular Dynamics Simulations"** Smith, K.D; Stoliarov, S.I.; Nyden, M.R.; Westmoreland, P.R.; *Molecular Simulation* 2007, Vol. 33, Nos. 4-5, 361-368.

5. **"Poly(arylate-phosphonate) copolymers with deoxybenzoin in the backbone: synthesis, characterization and thermal properties"** Ranganathan, T.; Ku, B-C; Zilberman, J.; Beaulieu, M.; Farris, R.J.; Coughlin, E.B.; Emrick, T. *Journal of Polymer Science, Part A: Polymer Chemistry*, 2007, *45*, 4573-4380.

6. **"Synthesis and characterization of halogen-free antiflammable polyphosphonates containing 4,4'- bishydroxydeoxybenzoin"** Ranganathan, T.; Zilberman, J.; Farris, R.J.; Coughlin, E.B.; Emrick, T., *Macromolecules* 2006, 39, 5974-5975.

7. **"Novel deoxybenzoin-based polyarylates as halogen-free fire-resistant polymers"** Ellzey, K.A.; Ranganathan, T.; Zilberman, J.; Coughlin, E.B.; Farris, R.J.; Emrick, T., *Macromolecules* 2006, 39, 3553-3558.

8. **"Enhanced crystallization of bisphenol-A polycarbonate by nano-scale clays in the presence of supercritical carbon dioxide"** Hu X.B.; Lesser A.J.; *Polymer* 2004, **45**(7):2333-2340

9. **"Fire-resistant polymers based on char formation rather than halogenation"** Ellzey, K.A.; Farris, R.J.; Emrick, T. *Polymer Preprints (American Chemical Society, Division of Polymer Chemistry)* 2004, 45 no.1, 939-940.

10. **"Post-treatment of poly-p-phenylenebenzobisoxazole (PBO) fibers using supercritical carbon dioxide"** Hu X.B.; Lesser A.J.; *Abstracts of Papers of the American Chemical Society* 2004, **227**:U562-U562.

11. **"Applications of reactive molecular dynamics to the study of the thermal decomposition of polymers and nanoscale structures"** Nyden, M.R.; Stoliarov, S.I.; Westmoreland, P.R.; Guo, Z.X.; Jee, C. *Materials Science and Engineering A-Structural Materials Properties Microstructure and Processing* 2004, 365 no.1, 114-121.

12. **"Modeling ethylene combustion from low to high pressure"** Carriere, T.; Westmoreland, P.R.; Kazakov, A.; Stein, Y.S.; Dryer, F.L. *Proceedings of the Combustion Institute* 2003, 29 no. 1, 1257-1266.

13. **"Synthetic and thermal studies of bisphenol-C containing poly(aryletherketone)"** Ellzey, K.A.; Farris, R.J.; Emrick, T. *Polymer Bulletin* 2003, 50 no.4, 235-242.

14. **"Synthesis of low heat release, high char thermoplastic polymers."** O'Donnell, P.M.; Yoo, E.S.; Farris, R.J.; Coughlin, E.B. *Abstracts of Papers of the American Chemical Society* 2003, 226:40-PMSE Part 2.

15. **"Mechanism of the thermal decomposition of bisphenol C polycarbonate: nature of its fire resistance"** Stoliarov, S.I.; Westmoreland, P.R. *Polymer* 2003, 44 no.18, 5469-5475.

16. **"A reactive molecular dynamics model of thermal decomposition in polymers: I. poly(methyl methacrylate)"** Stoliarov, S.I.; Westmoreland, P.R.; Nyden, M.R.; Forney, G.P. *Polymer* 2003, 44 no.3, 883-894.

17. **"Synthesis and characterization of the polyhydroxyamide/polymethoxyamide family of polymers"** Yoo, E.S.; Gavrin, A.J.; Farris, R.J.; Coughlin, E.B. *High Performance Polymers* 2003, 15 no.4, 519-535.

18. **"Low flammability and thermal decomposition behavior of Poly(3,3'-dihydroxybiphenylisophthalamide) and its derivatives"** Zhang, H.; Farris, R.J.; Westmoreland, P.R. *Macromolecules* 2003, 36 no. 11, 3944-3954.

19. **"Highly concentrated, intercalated silicate nanocomposites: Synthesis and characterization"** Zerda A.S.; Caskey T.C.; Lesser A.J.; *Macromolecules* 2003, **36**(5):1603-1608.

20. **"Synthesis and cyclization of aromatic polyhydroxyamides containing trifluoromethyl groups"** Baik, D.H.; Kim, H.Y.; Kantor, S.W. *Fibers and Polymers* 2002, 3 no.3, 91-96.

21. **"Characterization of two precursor polyblends: Polyhydroxyamide and poly(amic acid)"** Chang, J.H.; Farris, R.J. *Polymer Engineering and Science* 2002, 40 no.2, 320-329.

22. **"A reactive molecular dynamics model of thermal decomposition in polymers: I. Poly(methyl methacrylate)"** Stoliarov, S.I.; Westmoreland, P.R.; Nyden, M.R.; Forney, G.P. *Polymer* 2002, 44 no.3, 883-894.

23. **"Modeling and identifying intramolecular mechanisms of polymer degradation"** Westmoreland, P.R.; Stoliarov, S.I.; Zhang, H.Q.; Nyden, M.R. *Abstracts of Papers of the American Chemical Society* 2002, 223:516-PHYS Part 2.

24. **"Organophosphorous additive for fortification, processibility, and flame retardance of epoxy resins"** Zerda, A.S.; Lesser, A.J. *Journal of Applied Polymer Science* 2002, 84 no.2, 302-309.

25. **"Synthesis of UV-sensitive and fire-resistant polyarylates"** Plichta, A.; Brzozowski, Z. K.;, Zhang, H.:, Coughlin, E.B.; Westmoreland, P.R.; and Farris, R.J. *Polymer* 2002 43(20), 5463-5472.

26. **"Fire-resistant, UV/visible sensitive polyarylates and copolymers"** Zhang, H.; Coughlin, E.B.; Westmoreland, P.R.; Farris, R.J.; Plichta, A.; Brzozowski, Z.K. *Polymer Preprints (American Chemical Society, Division of Polymer Chemistry)* 2002, 43 no.1, 340-341.

27. **"Thermal decomposition and flammability of fire-resistant, UV/visible-sensitive polyarylates, copolymers and blends"** Zhang, H.; Westmoreland, P.R.; Farris, R.J.; Coughlin, E.B.; Plichta, A.; Brzozowski, Z.K. *Polymer* 2002, 43 no.20, 5463-5472.

28. **"Flammability kinetics from TGA/DSC/GCMS, microcalorimetry and computational quantum chemistry"** Westmoreland, P.R.; Inguilizian, T.; Rotem, K. *Thermochimica Acta* 2001, 367, 401-405.

29. **"Synthesis and characterization of fire-safe polymers"** Gavrin, A.J.; Yoo, E.S.; Farris, R.J.; Coughling, E. B. *Polymer Preprints (American Chemical Society, Division of Polymer Chemistry)* 2001, 42 no.2, 374-375.

30. **"Thermal decomposition and combustion behavior of poly(hydroxyamide) (PHA) and its derivatives"** Zhang, H.Q.; Westmoreland, P.R.; Farris, R.J. *Abstract Papers of the American Chemical Society* 2001, 222: 227-PMSE Part 2.

31. **"Pericyclic chemistry in polymer thermal decomposition"** Westmoreland, P.R.; and Rotem, K. *Foundations of Molecular Modeling and Simulations* 2001 (P.T. Cummings, P.R. Westmoreland, and B. Carnahan, eds.), AIChE Symposium Series No. 325, Vol. 97, 127-130.

32. **"Effect of heat treatment on the thermal and mechanical properties of polyhydroxyamic acid presursor films"** Park, S.K.; Farris, R.J. *Polymer Bulletin* 2000, 45 no.4, 405-410.

33. **"Vinyl-Substituted Silphenylene Siloxane Copolymers: Novel High-Temperature Elastomers"** Lauter, U.; Kantor, S.W.; Schmidt-Rohr, K.; MacKnight, W.J. *Macromolecules* 1999, 32 no.10, 3426-3431.

34. **"Evaluation of short term-high intensity thermal degradation of graphite fiber reinforced laminates via ultrasonic spectroscopy"** Schueneman, G.T.; Lesser, A.J.; Hobbs, T.R.; Novak, B.M. *Journal of Polymer Science, Part B: Polymer Physics* 1999, 37 no.18, 2601-2610

35. **"Developing polyhydroxamide as a low-flammability polymer: An interplay among computational chemistry, polymer synthesis, and kinetics data"** Westmoreland, P.R.; Rotem, K.; Inguilizian, T.; Gao, C.P.; Kantor, S.W.; Lyon, R.E. *Abstracts of Papers of the American Chemical Society* 1999, 217: 099-COMP Part 1.

36. **"Effect of heat treatment on the thermal and mechanical properties of a precursor polymer: polyhydroxyamide"** Chang, J.H.; Chen, M.J.; Farris, R.J. *Polymer* 1998, 39 no.23, 5649-5654.

37. **"The effect of network architecture on the thermal and mechanical behavior of epoxy resins"** Crawford, E.; Lesser, A.J. *Journal of Polymer Science, Part B: Polymer Physics* 1998, 36 no.8, 1371-1382.

38. **"Flame retarding properties of phosphorus containing poly(amic acid)"** Kim, H.J.; Choi, J.K.; Jo, B.W.; Chang, J.H.; Farris, R.J. *Korea Polymer Journal* 1998, 6 no.1, 84-90.

39. **"Synthesis, thermal and mechanical characterization of silphenylene vinylsiloxane elastomers"** Lauter, U.; Kantor, S.W.; Macknight, W.J. *Polymer Preprints (American Chemical Society, Division of Polymer Chemistry)* 1998, 39 no.1, 613-614.

40. **"Effect of TEMPO stable free radicals on the reduction of polymer flammability"** Stewart, J.R.; Novak, B.M.; Farris, R.J. *Polymer Preprints (American Chemical Society, Division of Polymer Chemistry)* 1998, 39 no. 2, 653-654.

41. **"Synthesis and characterization of latent fire retardant polymers: New tempo substituted polycarbodiimides"** Stewart, J.R.; Novak, B.M.; Farris, R.J. *Abstracts of Papers of the American Chemical Society* 1998, 215:018-PMSE Part 2.

42. **"Thermally Stable Silphenylene Vinyl Siloxane Elastomers and Their Blends"** Zhu, H.D.; Kantor, S.W.; MacKnight, W.J. *Macromolecules* 1998, 31 no. 3, 850-856.

Data on Scientific Collaborators

UMASS FACULTY

Professor Todd Emrick (principal investigator)

Professor Richard Farris

Professor E. Bryan Coughlin

Professor Alan Lesser

Professor Philip Westmoreland

STUDENTS AND POST-DOCTORAL RESEARCHERS

Jared Archer, UMass Amherst

Michael Beaulieu, UMass Amherst

Dr. Bon-Cheol Ku, UMass Amherst

Dr. Sung Cheal Moon, UMass Amherst

Dr. Andrey Pereverzev, UMass Amherst

Thangamani Ranganathan, UMass Amherst

Dr. Beom Young Ryu, UMass Amherst

Kenneth Smith, UMass Amherst

Jian Wu, UMass Amherst

Dr. Joseph Zilberman, UMass Amherst

Information on Inventions

1. **"Deoxybenzoin based antiflammable polyphosphonates and poly(arylate-phophonate) copolymer compounds, compositions and related methods of use" Emrick, T.; Ranganathan, T.; Coughlin, E.B.; Farris, R.J.; Zilberman, J.; U.S. Patent Provisional application: USSN 60/834,848 filed August 1, 2006, ; US Patent Application: USSN 11/888,504, filed August 1, 2007.**

United States Patent Application	**20080033144**
Kind Code	**A1**
Emrick; Todd ; et al.	**February 7, 2008**

ABSTRACT

Deoxybenzoin-phosphonate and other copolymer compounds, compositions and related methods.

Inventors:	*Emrick*; Todd; *(Deerfield, MA)* ; Ranganathan; T.; *(Amherst, MA)* ; Coughlin; E. Bryan; *(Amherst, MA)* ; Farris; Richard J.; *(Leeds, MA)* ; Zilberman; Joseph; *(Haifa, IL)*
Correspondence Name and Address:	REINHART BOERNER VAN DEUREN S.C.;ATTN: LINDA KASULKE, DOCKET COORDINATOR 1000 NORTH WATER STREET SUITE 2100 MILWAUKEE, WI 53202 US
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2. **"Deoxybenzoin-Derived Anto-Flammable Polymers" Emrick, T.; Coughlin, E.B.; Ku, B-C; Ranganathan, T.; Beaulieu, M.; Farris, R.J.; U.S Patent Application: USSN 61/072,517 filed March 31, 2008.**

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Applicants: UNIVERSITY OF MASSACHUSETTS [US/US]; President's Office, UMass 12th Floor 225 Franklin Street Boston, MA 02110 (US) *(All Except US)*.
EMRICK, Todd [US/US]; (US) *(US Only)*.
COUGHLIN, E., Bryan [US/US]; (US) *(US Only)*.
RANGANATHAN, Thangamani [IN/US]; (US) *(US Only)*.
BEAULIEU, Michael [US/US]; (US) *(US Only)*.
FARRIS, Richard [US/US]; (US) *(US Only)*.