

SPE/ACS/ASM/AIChE Joint Technical Society Dinner Meeting
Thursday, June 15, 2006

GRAPHENE NANO SHEETS AS A NEW MATERIAL FOR POLYMER COMPOSITES

Prof. Robert K. Prud'homme, Director of the Engineering Biology Program and Professor in the Department of Chemical Engineering, Princeton University, Princeton, NJ 08544

Abstract: There has been considerable interest and activity in the area of nanoparticle-filled polymer composites because of the predicted enhancement in mechanical, electrical, and transport properties. Carbon nanotubes and clay nanosheets have been the most widely studied materials, but each has significant limitations. We present a new nanofiller based on completely exfoliated graphite sheets. The process for exfoliation will be described, as well as characterization of the resulting TEGO (thermally exfoliated graphite oxide). Surface areas of 1500 m²/g are obtained and aspect ratios on the order of 10⁴ (i.e., 10 microns/1 nm) are obtained. The electrically conductive sheets show a percolation threshold between 1-2 wt% when incorporated in a poly(methyl methacrylate) (PMMA) polymer matrix. This is in contrast to 7.5 wt% loading of conductive carbon black that must be added to obtain a similar level of conductivity. The elastic modulus versus temperature for a TEGO-filled PMMA composite shows an increase. But most significantly, the addition of just 0.25 wt% TEGO increases the softening temperature (or glass transition temperature T_g) from 95°C to 118°C. This change is unprecedented at this filler loading. The shift in T_g of the matrix polymer means that the TEGO is well enough dispersed so that "every" PMMA chain is influenced by the TEGO surface. Therefore, the bulk polymer properties are modified by very low loadings of TEGO.

Presenter: Prof. Robert K. Prud'homme, Director of the Engineering Biology Program and Professor in the Department of Chemical Engineering, Princeton University, and the 2006 MMI Turner Alfrey Visiting Professor.

Date: Thursday, June 15, 2006

Time: Social 6:30 PM
Dinner 7:00 PM
Program 8:00 PM

Location: Holiday Inn of Midland, 1500 W. Wackerly St., Midland, MI 48640, 989-631-4220

Cost: \$25.00 for SPE/ACS/ASM/AIChE members and guests
\$15.00 for students

Reservations: Reservations can be made via phone, fax, or e-mail to Dawn Wright at MMI. They must be received no later than Monday, June 12, 2006.
Phone: 989-832-5555, ext. 570, Fax: 989-832-5560
E-mail: wright@mmi.org

2006 Turner Alfrey Visiting Professor Course

COURSE 1033: STRUCTURE AND DYNAMICS OF COMPLEX, ASSOCIATING, NANO-SCALE SYSTEMS

Lecturer: Professor Robert K. Prud'homme, Director of the Engineering Biology Program and Professor in the Department of Chemical Engineering, Princeton University

Place: Lecture Hall (Room 101), Michigan Molecular Institute, 1910 West St. Andrews Road, Midland, MI 48640

Time: Formal lectures: Monday – Friday, June 12 – 16, 2006, 3:00 – 6:00 p.m.

Fee: There is no fee for auditors if they belong to organizations that are financial sponsors of the Turner Alfrey Visiting Professor Program – Dow Chemical, Dow Corning, Saginaw Valley State University, Central Michigan University, Michigan State University, and Mid-Michigan Section of the SPE. For all others, a course fee of \$300 will be required at registration.

All participants must register.

Registration: Pre-registration is required one week in advance with the Registrar by calling (989) 832-5555, ext. 555 or by e-mail at registrar@mmi.org.

LECTURE TOPICS:

Lecture 1 – Monday, June 12, 2006 – “Block Copolymer Mediated Nanoparticle Formation”

A novel process involving tuning rapid nucleation and growth of a hydrophobic solute (drug, agricultural active, pigment, or gold nanoparticle) will be described. The kinetics of self-assembly of a block copolymer controls the particle size. Tunable conjugation of the active species enables controlled release from the nanoparticle formulation.

Lecture 2 – Tuesday, June 13, 2006 – “Polymer-Surfactant Interactions: Thermodynamics and Dynamics”

Complex interactions between self-assembling surfactant mesophases and polymers can be used to tune rheology and control phase behavior. Interactions can be enthalpic or entropic, and are sensitively controlled by interactions at nanometer length scales.

Lecture 3 – Wednesday, June 14, 2006 – “Self-Assembly in Non-Aqueous Media Using Crystallinity”

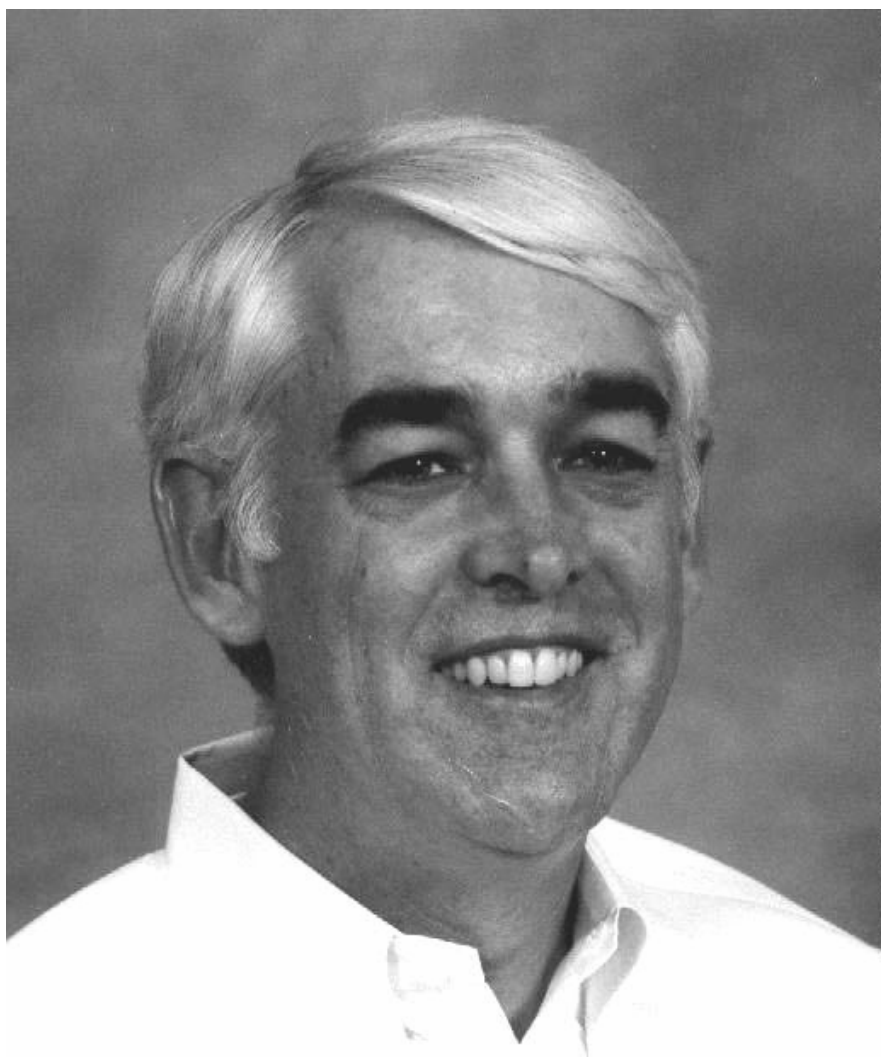
Prevention of gelation of waxes in oil phases is increasingly important in deep, off-shore oil production. Polymers that provide steric stabilization of wax crystals must co-crystallize with the wax phase, since polarity cannot drive self-assembly. Neutron scattering complements rheology to guide the synthesis of the correct polymer structure.

Lecture 4 – Thursday, June 15, 2006 – “Single Sheet Graphene Nano Composites”

The promise of nano composites is that if filler length scales are comparable to polymer dimensions then dramatic changes in composite properties can be achieved. A process to produce single graphene sheets creates a nano filler that produces superior nano composite materials.

Lecture 5 – Friday, June 16, 2006 – “Living Polymers: Self-Assembling Worm-like Micelles”

Small molecule amphiphiles assemble into geometries with unique structures and dynamics. Worm-like micelles produce “living” polymeric networks that obey remarkably simple laws. The flow of these micelles into small pores produces some important surprises.



Professor Robert K. Prud'homme

**Director of the Engineering Biology Program and
Professor in the Department of Chemical Engineering,
Princeton University, Princeton, NJ 08544**

**2006 Turner Alfrey Visiting Professor
Michigan Molecular Institute, Midland, MI 48640**

Biographical Sketch of Prof. Robert K. Prud'homme

Robert K. Prud'homme is a Professor in the Department of Chemical Engineering, and Director of the Engineering Biology Program at Princeton University. He received a BS degree in Chemical Engineering from Stanford University in 1969, and a PhD degree in Chemical Engineering from the University of Wisconsin-Madison in 1978, studying under Professor Robert Bird. He also completed a Graduate Studies Program in Environmental Science and Public Policy at Harvard University in 1973.

Prof. Prud'homme has served on the executive committees of the Materials Science Division of the American Institute of Chemical Engineers, and the U.S. Society of Rheology. He is also currently Vice President of the U.S. Society of Rheology. He has also served as the Chair of the Technical Advisory Board for Materials Science Research for The Dow Chemical Company, and was on the Board of Directors of Rheometric Scientific, Inc., the leading manufacturer of rheological instrumentation.

His awards include the NSF Presidential Young Investigator Award, the Princeton School of Engineering and Applied Science Outstanding Teaching Award, the Sydney Ross Lectureship at Rensselaer Polytechnic Institute, the Bird, Stewart and Lightfoot Lecturer at the University of Wisconsin, and the Turner Alfrey Visiting Professorship at the Michigan Molecular Institute.

Prof. Prud'homme has been the Organizer and Chair of the Gordon Conference on Ion Containing Polymers, and the Society of Petroleum Engineers Forum on Stimulation Fluid Rheology, in addition to organizing numerous sessions at AIChE, ACS, and Society of Rheology meetings. He is currently the Director of the Princeton–University of Minnesota–Iowa State NSF NIRT (Nanoscale Interdisciplinary Research Teams) Center on Nanoparticle Formation.

His research interests include rheology and self-assembly of complex fluids, and his particular systems of interest include biopolymer solutions and gels, surfactant mesophases, and polymer/surfactant mixtures. The goals of Prof. Prud'homme's studies are to understand how weak molecular-level interactions can be used to tune macroscopic bulk properties and phase behavior, and the outcome of his work has resulted in more than 200 publications to date.

BIOGRAPHY – PROF. ROBERT K. PRUD’HOMME

CURRENT POSITION

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EDUCATION

1969	BS	Chemical Engineering	Stanford University
1973		Graduate Studies Program	Harvard University
		Environmental Science and Public Policy	
1978	PhD	Chemical Engineering	University of Wisconsin-Madison

MILITARY EXPERIENCE

1969-1972	Officer (Captain), U.S. Army, Republic of Vietnam (1970-1971)
1971-1972	Environmental Engineer, U.S. Army Armaments Command, Joliet, IL

Awards: Bronze Star, Army Commendation Medal

HONORS AND ACTIVITIES

- National Science Foundation, Presidential Young Investigator Award (1984)

Visiting Professorships and Lectureships

- University of Sydney Visiting Professor Fellowship (2006)
- Turner Alfrey Visiting Professor, Michigan Molecular Institute (2006)
- Bird, Stewart and Lightfoot Lecturer, University of Wisconsin (2005)
- McCabe Lecturer, Department of Chemical Engineering, North Carolina State University (1992)
- Lecturer, Polymer Processing Institute short course, "Polymers in Electronics Packaging", Princeton, NJ (1988)
- Lecturer, ACS short course, "Water-Soluble and Water-Swellable Polymers", Division of Polymeric Materials Science and Engineering (1986, 1987, 1992, 1993)
- Lecturer, University of Minnesota short course, "Rheological Measurements", Minneapolis, MN (1985)
- Lecturer, University of Connecticut short course, "Laser Doppler Velocimetry", Storrs, CT (1985)

Editorial Advisory Boards

- Editorial Board, "Polymer Gels and Networks", Elsevier Science Publishers (1992-present)
- Editorial Board, Series in Chemical Engineering, Butterworths Publishers (1983-present)

Professional Society Service

- Vice President, Society of Rheology (2005)
- Executive Committee, U.S. Society of Rheology (1989-1991)
- Board of Directors, AIChE, Materials Science and Engineering Division (1982-1992)

Professional Society Symposia Chairmanships

- Session Chairman, American Chemical Society, Division of Polymeric Materials Science and Engineering, “Polymeric Surfactants,” New Orleans, LA (1999)
- Session Chairman, Gordon Conference, “Ion Containing Polymers” (1999)
- Session Chairman, Materials Research Society, Spring Meeting (1999)
- Session Organizer, American Chemical Society, Division of Polymeric Materials Science and Engineering, “Water-Soluble/Water-Swellable Polymers,” Boston, MA (1998)
- Session Chairman, American Chemical Society, Division of Colloid and Surface Chemistry, “Associating Polymers in Aqueous Media,” Boston, MA (1998)
- Session Chairman, American Chemical Society, “Polymer Surfactant Interactions, Gels and Phase Behavior,” San Francisco, CA (1997)

Service to Industry

- BASF Advisory Council for Nanotechnology (2005)
- Advisory Committee, Water Soluble Polymer Research, American Cyanamid Central Research, Stamford, CT (1985)
- Board of Directors, Rheometric Scientific, Inc., Piscataway, NJ (1982-present)
- Task Force on Exxon Research and Engineering University Cooperative Research, Florham Park, NJ (1979-1981)

Service to Academe and Government

- Wayne State University Visiting Committee (2005)
- Operations Advisory Group, New Jersey Center for Biomaterials & Devices (1997)
- Director, Program in Engineering Biology, Princeton University (1990-present)
- Steering Committee, National Bureau of Standards, Chemical Engineering Center Mixing Study, Boulder, CO (1984)

RECENT PUBLICATIONS

- “pH Triggered Release of Protective Poly(Ethylene Glycol)-b-Polycation Copolymers from Liposomes”, D.T. Auguste, S.P. Armes, K.R. Brzezinska, T.J. Deming, J. Kohn, and R.K. Prud’homme, *Biomaterials*, in print (2006).
- “Novel Associative Polymer Networks Based on Cyclodextrin Inclusion Compounds”, X. Guo, A.A. Abdala, B.L. May, S.F. Lincoln, S.A. Khan, and R.K. Prud’homme, *Macromolecules*, **38**, (7), 3037-3040, (2005).
- “Interaction of Paraffin Wax Gels with Ethylene/Vinyl Acetate Co-Polymers”, H.S. Ashbaugh, X. Guo, D. Schwahn, R.K. Prud’homme, D. Richter, and L.J. Fetters, *Energy and Fuels*, **19**, (1), 138-144, (2005).
- “Polymer-Protected Liposomes: Association of Hydrophobically-Modified PEG with Liposomes”, D. Auguste, P. Ahl, P. Meers, J. Kohn, and R.K. Prud’homme, in *Polymeric Drug Delivery Volume I – Particulate Drug Carriers*, Svenson, S. (Ed.), ACS Symposium Series, **923**, American Chemical Society, Washington, DC, submitted (2005).
- “Effect of Hydrophobically Modified Polymers on Shear-Induced Multilamellar Vesicles” B.S. Yang, W.B. Russel, and R.K. Prud’homme, *Langmuir*, **21**, (22), 10038-10045, (2005).
- “Effect of Cooling Rate on Crystallization of Model Waxy Oils with Microcrystalline Poly(ethylene-butene)”, X. Guo, B.A. Pethica, J.S. Huang, and R.K. Prud’homme, *Energy & Fuels*, published online Nov. 25, (2005).
- “NanoPrecipitation of Pharmaceuticals Using Mixing and Block Copolymer Stabilization”, B.K. Johnson, W. Saad, and R.K. Prud’homme, in *Polymeric Drug Delivery Volume II – Polymeric*

- Matrices and Drug Particle Engineering*, Svenson, S. (Ed.), *ACS Symposium Series*, **924**, submitted (2005).
- “Latex Composite Membranes: Structure and Properties of the Discriminating Layer”, S. Ramakrishnan, C.J. McDonald, R.K. Prud’homme, and J.D. Carbeck, *Journal of Membrane Science*, **231**, (1-2), 57-70 (2004).
 - “Crystallization of mixed paraffin from model waxy oils and the influence of micro-crystalline poly(ethylene-butene) random copolymers”, Guo, X.H., Pethica, B.A., Huang, J.S., Prud’homme, R.K., Adamson, D.H. and Fetters, L.J., *Energy & Fuels*, **18**, (4) 930-937 (2004).
 - “Crystallization of long-chain n-paraffins from solutions and melts as observed by differential scanning calorimetry”, Guo, X.H., Pethica, B.A., Huang, J.S. and Prud’homme, R.K., *Macromolecules*, **37**, (15), 5638-5645, (2004).
 - “Differential scanning calorimetry studies of clathrate hydrate formation”, Zhang, Y.F., Debenedetti, P.G., Prud’homme, R.K. and Pethica, B.A., *Journal of Physical Chemistry B*, **108**, (43), 16717-16722, Oct. 28, (2004).
 - “Diffusion of compact macromolecules through polymer meshes: Mesh dynamics and probe dynamics”, Biehl, R., Guo, X., Prud’homme, R.K, Monkenbusch, M., Allgeier, J. and Richter, D., *Physica B*, **350**, (1-3) 76-78, (2004).
 - “Effects of Organic Solvents on the Scission Energy of Rodlike Micelles”, Siriawatwechakul, W., LaFleur, T., Prud’homme, R.K., and Sullivan, P., *Langmuir*, **20**, (21), 8970-8974, (2004).
 - “Model associative polymer networks generated by inclusion interaction between polymers with cyclodextrin and hydrophobic grafts”, Guo, X., Abdala, A.A., Prud’homme, R.K., Lincoln, S.F. and Khan, S.A., *ACS Polymer Preprints*, **45**, (2), 602-603, (2004).
 - “Diffusion of protein in polymer solutions: A comparison between neutron spin-echo spectroscopy and NMR measurement”, Guo, X., Biehl, R., Pacheco, C.R., Monkenbusch, M., Richter, D., Fu, L. and Prud’homme, R.K., *ACS Polymer Preprints*, **45**, (2), 788-789, (2004).
 - “Preparation of biocompatible hydrogel adhesives controlled by rheological method”, Guo, X., Prud’homme, R.K., Deng, F., Leth, S.J., Nunalee, N. and Shull, K.R., *ACS Polymer Preprints*, **45**, (2), 604-605, (2004).
 - “Influence of micro-crystalline poly(ethylene-butene) random copolymers on wax gelation of black oils”, Guo, X., Pethica, B.A., Adamson, D.A., Tinsley, J., Huang, J.S. and Prud’homme, R.K., *Preprints, American Chemical Society, Division of Petroleum Chemistry*, **49**, (4), 388-389, (2004).
 - “Synthesis of poly(ethylene-butene) random copolymers with hydroxylic grafts and effect of polar groups on deposition of wax and asphaltenes from crude oil”, Guo, X., Adamson, D.A., Tinsley, J., Pethica, B.A., Huang, J.S. and Prud’homme, R.K., *Preprints, American Chemical Society, Division of Petroleum Chemistry*, **49**, (3), 272-273, (2004).
 - “Mechanism for Rapid Self-Assembly of Block Copolymer Nanoparticles”, B.K. Johnson and R.K. Prud’homme, *Physical Review Letters*, **91**, (11), 118302 (2003).
 - “Chemical Processing and Micromixing in Confined Impinging Jets”, B.K. Johnson and R.K. Prud’homme, *AIChE Journal*, **49**, (9), 2264-2282 (2003).
 - “Flash NanoPrecipitation of Organic Actives and Block Copolymers Using a Confined Impinging Jets Mixer”, B.K. Johnson and R.K. Prud’homme, *Australian Journal of Chemistry*, **56**, (10), 1021-1024 (2003).
 - “Diffusion of Compact Macromolecules Through Polymer Meshes: Mesh Dynamics and Probe Dynamics” R. Biehl, G. Xuehong, R.K. Prud’homme, M. Monkenbusch, J. Allgeier, D. Richter, submitted to Elsevier Science (2003).
 - “Association of Hydrophobically-Modified Poly(Ethylene Glycol) with Fusogenic Liposomes”, D.T. Auguste, R.K. Prud’homme, P.L. Ahl, P. Meers and J. Kohn, *Biochimica et Biophysica ACTA*, **1616**, (2), 184-195 (2003).
 - “Stabilization of Phosphatidylserine/Phosphatidylethanolamine Liposomes with Hydrophilic Polymers Having Multiple “Sticky Feet”, M.L. Hwang, R.K. Prud’homme, J. Kohn, and J.L. Thomas, *Langmuir*, **17**, 7713-7716 (2002).

- “Interaction of Hydrophobically Modified Polymers and Surfactant Lamellar Phase”, B.S. Yang, J. Lal, P. Richetti, C.M. Marques, W.B. Russel, and R.K. Prud’homme, *Langmuir*, **17**, 5834-41 (2001).
- “Interaction of Surfactant Lamellar Phase and a Strictly Alternating Comb-Graft Amphiphilic Polymer Based on PEG”, B.S. Yang, J. Lal, J. Kohn, W.B. Russel, and R.K. Prud’homme, *Langmuir*, **17**, 6692-98 (2001).
- “Stability and Behavior of a Comb-graft Copolymer Stabilizing a Thin Oil Emulsion Film”, M.R. Anklam, D.A. Saville, R.K. Prud’homme, *Polym. Adv. Technol.*, **12**, 70-84 (2001).
- “Cure Depth in Photopolymerization: Experiments and Theory”, J.H. Lee, R.K. Prud’homme, and I.A. Aksay, *J. Mater. Res.*, **16** (12), 3536-3544 (2001).
- “Enzymatic Degradation of Guar and Substituted Guar Galactomannans”, Y. Cheng, R.K. Prud’homme, *Biomacromolecules*, **1**, 782 (2000).
- “Behavior of Kappa-Carrageenan in Glycerol and Sorbitol Solutions”, S. Ramakrishnan and R.K. Prud’homme, *Carbohydrate Polymers*, **43**, (4), 327-332 (2000).
- “Dynamic deformation visualization in swelling of polymer gels”, E.C. Achilleos, R.K. Prud’homme, K.N. Christodoulou, K.R. Gee, I.G. Kevrekidis, *Chemical Engineering Science*, **55**, 3335-3340 (2000).