Final Report

Title: "Reducing energy consumption and pollution in plastic-manufacturing processes: Phase-behavior roots of fouling phenomena that cause energy and product waste in manufacturing of ethylene copolymers"

U.S. Department of Energy Grant No. DE-FG02-96ER12201.A00
Recipient: Louisiana State University, Baton Rouge, LA 70803-4001
Budget and project period: from 9-15-96 to 9-14-99

PI: M. Radosz, M. F. Gautreaux/Ethyl Chaired Professor
Department of Chemical Engineering and Macromolecular Studies Group
Louisiana State University, Baton Rouge, LA 70803-7303

Graduate Students:

Hertanto Adidharma, Ph.D. 1999
Alan Chan, Ph.D. 1999
Cheng Pan, M.S. 1997
Y. C. Kuo, M.S. 1999

DOE Patent Clearance Granted

MP Dvorscak

7.16.03

Mark P. Dvorscak

Date

(630) 252-2393

E-mail: mark.dvorscak@ch.doe.gov

Office of Intellectual Property Law

DOE Chicago Operations Office

Postdoctoral Associates:

Heng Shi
Marek Luszczyk

Goal: To understand the phase behavior of ethylene copolymers in compressible fluid streams, such as copolymer solutions in supercritical and near critical fluids.

Incentive: Such understanding is needed to develop new plastic-manufacturing processes that are less energy intensive, and produce less pollution and less waste product, for example, to control undesirable phase transitions and, hence, eliminate the root cause of fouling phenomena in pipelines, reactors and separators.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Approach: A synthesis of experiment and thermodynamic modeling. The experiments are aimed at accurate phase transition data for well characterized model polyolefin systems. The thermodynamic modeling is aimed at predicting such phase transitions.

Summary of Technical Accomplishments:

- (1) The most significant accomplishment of this project is development of a new equation of state, referred to as SAFT1, on the basis of square-well formalism within the statistical associating fluid theory. SAFT1 is becoming our premier thermodynamic model for polymer systems in this project, but it has the potential of a powerful generic polymer equation of state.
- (2) A high-pressure light-scattering probe has been developed for polymer solutions in supercritical and nearcritical fluids, and used to study critical points in poly(ethylene-co-hexene-1) solutions in propane.
- (3) A study on modeling phase behavior of alkanes and polyolefins with copolymer SAFT has been completed.
- (4) A study on solid-liquid equilibria that underlie fouling has been completed.
- (5) A novel analytical method of fractionating polymers with respect to crystallinity distribution has been developed (patent application).

The work supported by this grant has been documented in twenty one refereed publications, one patent disclosure, and presented at numerous meetings and seminars:

Refereed publications (reprints attached)

Pan, C.; Radosz M. "Copolymer-SAFT Modeling of Phase Behavior in Hydrocarbon-Chain Solutions: Alkane Oligomers, Polyethylene, Poly(ethylene-co-Olefin-1), Polystyrene, and Poly(ethylene-co-Styrene)" *Ind. Eng. Chem. Res.* **1998**, *37*, 3169-3179.

Adidharma, H.; Radosz M. "Square-Well SAFT Equation of State for Homopolymeric and Heteropolymeric Fluids" *Fluid Phase Equilibria* **1999**, *158-160*, 165-174.

Adidharma, H.; Radosz M. "A Prototype of an Engineering Equation of State for Hetero-Segmented Polymers" *Ind. Eng. Chem. Res.* **1998**, *37*, 4453-4462.

Pan, C.; Radosz M. "SAFT Modeling of Solid-Liquid Equilibria in Naphthalene, Normal-Alkane and Polyethylene Solutions" *Fluid Phase Equilibria* **1999**, *155*, 57-73.

Adidharma, H.; Radosz M. "A Study of Square-Well Statistical Associating Fluid Theory Approximations" *Fluid Phase Equilibria* **1999**, *161*, 1-20.

Chan, A. K.; Hemmingsen, P. V.; Radosz, M. "Fluid-Liquid and Fluid-Solid Transitions of Tetracontane in Propane" *J. Chem. Eng. Data* **2000**, *45*, 362-368.

Chan, A. K.; Russo, P. S.; Radosz, M. "Fluid-Liquid Equilibria in Poly(ethylene-co-hexene-1) + Propane: A Light Scattering Probe of Cloud-Point Pressure and Critical Polymer Concentration" *Fluid Phase Equilibria* **2000**, *173*, 149-158.

Refereed publications with a partial support (reprints available upon request)

Pan, C.; Radosz M. "Phase Behavior of Poly(ethylene-co-hexene-1) Solutions in Isobutane and Propane" *Ind. Eng. Chem. Res.* **1999**, *38*, 2842-2848.

S. J. Han, D. J. Lohse, M. Radosz, L. H. Sperling "Preparation of a Thermoplastic Interpenetrating Polymer Network (IPN) from Isotactic Polypropylene and EPDM Terpolymer in Supercritical Propane" *ACS Polym. Prep.* **1997**, *38*, 2, 432-3.

Han, S. J.; Gregg, C. J.; Radosz, M. "How the Solute Polydispersity Affects the Cloud-Point and Coexistence Pressures in Propylene and Ethylene Solutions of Alternating Poly(ethylene-co-Propylene)" *Ind. Eng. Chem. Res.* **1997**, *36*, 5520-5525.

Chen, C. K.; Banaszak, M.; Radosz, M. "Statistical Associating Fluid Theory Equation of State with Lennard-Jones Reference Applied to Pure and Binary *n*-Alkane Systems" *J. Phys. Chem. B* **1998**, *102*, 2427-2431.

Han, S. J.; Lohse, D. J.; Radosz, M.; Sperling L. H. "Short Chain Branching Effect on the Cloud-Point Pressures of Ethylene Copolymers in Subcritical and Supercritical Propane" *Macromolecules* **1998**, *31*, 2533-2538.

Han, S. J.; Lohse, D. J.; Radosz, M.; Sperling L. H. "Thermoplastic Vulcanizates from Isotactic Polypropylene and EPDM in Supercritical Propane: Synthesis and Morphology" *Macromolecules* **1998**, *31*, 5407-5414.

Han, S. J.; Lohse, D. J.; Radosz, M.; Sperling, L. H. "Phase Behavior and Morphology of Polyolefin Blends and Thermoplastic Vulcanizates in Supercritical Propane", ICI Student Award Symposium in Applied Polymer Science, *Polym. Mater. Sci. Eng.* **1998**, *79*, 134-135.

Gregg, C. J.; Stein, F. P.; Radosz, M. "Phase Behavior of Telechelic Polyisobutylene in Subcritical and Supercritical Fluids. 4. SAFT Association Parameters from FTIR for Blank, Monohydroxy, and Dihydroxy PIB200 in

Ethane, Carbon Dioxide and Chlorodifluoromethane" *J. Phys. Chem. B* **1999**, *103*, 1167-1175.

Chen, A. Q.; Radosz, M. "Phase Equilibria of Dilute Poly(ethylene-co-1-butene) Solutions in Ethylene, 1-Butene, and 1-Butene+Ethylene" *J. Chem. Eng. Data* **1999**, *44*, 854-859.

Kinzi, M.; Luft, G.; Adidharma, H.; M. Radosz "SAFT Modeling of Inert-Gas Effects on the Cloud-Point Pressures In Ethylene Copolymerization Systems: Poly(ethylene-co-Vinyl Acetate)+Vinyl Acetate+Ethylene and Poly(ethylene-co-Hexene-1)+Hexene-1+Ethylene with Carbon Dioxide, Nitrogen, or n-Butane" *Ind. Eng. Chem. Res.* **2000**, *39*, 541-546.

Chan, A. K.; Adidharma, H.; Radosz, M. "Fluid-Liquid and Fluid-Solid Transitions of Poly(ethylene-co-octene-1) in Sub- and Supercritical Propane Solutions" *Ind. Eng. Chem. Res.* **2000**, *39*, 3069-3075.

Chan, A. K.; Adidharma, H.; Radosz, M. "Fluid-Liquid Transitions of Poly(ethylene-co-octene-1) in Supercritical Ethylene Solutions" *Ind. Eng. Chem. Res.* **2000**, *39*, 4370-4375.

Chan, A. K.; Radosz, M. "Phase Behavior of Poly(ethylene-co-hexene-1) Solutions in Sub- and Supercritical Propane, Ethylene, and Ethylene+1-Hexene" *Macromolecules* **2000**, *33*, 6800-6807.

Han, S. J.; Lohse, D. J.; Radosz, M.; Sperling, L. H. "Morphology of Blends of Polypropylene and Ethylene-Butene Copolymer by Rapid Expansion of Supercritical Solution and Isobaric Crystallization from Supercritical Solution", *J. Appl. Polym. Sci.* **2000**, *77*, 1478-1487.

Patent disclosure (Louisiana State University, November 12, 1997)

M. Radosz "Fractionation Method for Determining Crystallinity Distribution in Polymers"

Presenations

S. J. Han, D. J. Lohse, M. Radosz, L. H. Sperling "Preparation of a Thermoplastic Interpenetrating Polymer Network (IPN) from Isotactic Polypropylene and EPDM Terpolymer in Supercritical Propane" American Chemical Society Meeting, Las Vegas, September 7-11, 1997.

M. Radosz, "Macromolecular Thermodynamics of Polyolefin Systems" AspenWorld 97 International Conference, Boston, October 12-15, 1997. (invited)

M. Radosz, "Macromolecular Thermodynamics of Polyolefin Systems" American Institute of Chemical Engineers, Baton Rouge Section Meeting, November 10, 1997.

S. J. Han, D. J. Lohse, M. Radosz, L. H. Sperling "Phase behavior and Morphology of Polyolefin Blends and Thermoplastic Vulcanizates in Supercritical Propane" American Chemical Society Meeting, Boston, 1998.

M. Radosz, "Polymer Thermodynamics" Department of Chemical Engineering, Auburn University, Auburn, February 27, 1998. (invited)

M. Radosz, "Macromolecular Phase Equilibria: Metallocene-Catalyzed Polyolefins" School of Chemical Engineering, Purdue University, West Lafayette, March 19, 1998. (invited)

H. Adidharma, M. Radosz, "Square-Well SAFT Parameters and Equations of State for Homopolymeric and Heteropolymeric Fluids" AIChE Spring National Meeting, New Orleans, March 8-12, 1998, paper 64c.

A. K. Chan, M. Radosz, "Bubble, Dew, and Solid-Liquid Phase Transitions of Poly(ethylene-co-hexene-1) in Ethylene+Hexene-1 Solutions and in Propane Solutions" AIChE Spring National Meeting, New Orleans, March 8-12, 1998, paper 66b.

H. Adidharma, M. Radosz, "Square-Well SAFT Equation of State for Homopolymeric and Heteropolymeric Fluids" Eighth International

Conference on Properties and Phase Equilibria for Product and Process Design, April 26 - May 1, 1998, Noordwijkerhout, The Netherlands.

M. Radosz, "Thermodynamics of Metallocene-Catalyzed Polyolefins" Norwegian University of Technology, SINTEF, April 23, 1998, Trondheim, Norway. (invited)

M. Radosz, "Phase Behavior of Polymer Solutions in Near- and Supercritical Fluids" Department of Industrial Chemistry, Nihon University, Japan, July 23, 1998. (invited)

M. Radosz, "Phase Behavior of Polymer Solutions in Near- and Supercritical Fluids" Department of Chemical Engineering, Tohoku University, Japan, July 24, 1998. (invited)

M. Radosz, "Phase Behavior of Polymer Solutions in Near- and Supercritical Fluids" Japan Society for the Promotion of Science Lecture, Hakone, Japan, July 28, 1998. (invited)

M. Radosz, "New Developments in High-Pressure Phase Equilibria of Polymer Systems (Measurement and Theory)" Lecture at Mitsui Chemical Company, Ohtake, Japan, July 30, 1998. (invited)

M. Radosz, "Phase Behavior of Polymer Solutions in Near- and Supercritical Fluids" Department of Chemical Engineering, Hiroshima University, Japan, July 31, 1998. (invited)

M. Radosz, "New Developments in High-Pressure Phase Equilibria of Polymer Systems (Measurement and Theory)" Lecture at Mitsubishi Chemical Company, Mizushima Plant, 4 August 1998. (invited)

M. Radosz, "Phase Behavior of Polymer Solutions in Near- and Supercritical Fluids" Department of Applied Chemistry and Biochemistry, Kumamoto University, Japan, August 6, 1998. (invited)

M. Radosz, "Phase Behavior of Polymer Solutions in Near- and Supercritical Fluids" Department of Chemical Systems and Engineering, Kyushu University, Japan, August 7, 1998. (invited)

M. Radosz, "Macromolecular Thermodynamics" Gautreaux Lecture,
Louisiana State University, September 11, 1998.

M. Radosz, "Phase Behavior of Metallocene-Catalyzed Ethylene Copolymer
Solutions in Sub- and Supercritical Fluid Solutions" Department of Polymer
Science, University of Southern Mississippi, May 5, 1999.

M. Radosz, "Thermodynamic Modeling of Liquid-Liquid and Solid-Liquid
Equilibria in Poly(ethylene-co-octene-1) Systems: Experimental Data and
Correlation" The Dow Chemical Company, Freeport, Texas, July 19, 1999.
(invited)

M. Radosz, "SAFT Modeling of Poly(ethylene-co- α -olefin) Systems"
AspenWorld 2000 Conference, Orlando, Florida, February 6-10, 2000.
(invited)