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# SGER: Supercritical Levitation Polymerization and Processing

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**Final Report for Period:** 05/1993 - 10/1995

**Submitted on:** 12/09/2004

**Principal Investigator:** Kiran, Erdogan .

**Award ID:** 9310232

**Organization:** University of Maine

**Title:**

SGER: Supercritical Levitation Polymerization and Processing

### Project Participants

#### Senior Personnel

**Name:** Kiran, Erdogan

**Worked for more than 160 Hours:** Yes

**Contribution to Project:**

#### Post-doc

#### Graduate Student

#### Undergraduate Student

#### Technician, Programmer

#### Other Participant

#### Research Experience for Undergraduates

### Organizational Partners

### Other Collaborators or Contacts

### Activities and Findings

**Research and Education Activities:** (See PDF version submitted by PI at the end of the report)

#### **Findings:**

Densities of binary fluid mixtures of organic liquid solvents such as pentane and toluene with carbon dioxide or with sulfur hexafluoride can be readily adjusted by pressure. These binary fluid mixtures can be used as levitation polymerization medium. Adjusting the density of polymerization medium to that of the polymer being produced was found to delay or prevent polymer precipitation, thereby leading to large increases in the molecular weight of the polymer formed. This was specifically demonstrated for polymerization of styrene in binary mixtures of carbon dioxide and sulfur hexafluoride by maintaining the density at about 1.05 gcm<sup>-3</sup>.

#### **Training and Development:**

Two graduate students and one postdoctoral fellow participated in different stages of this project. Significant research experience was gained in working with multicomponent reactive (undergoing polymerization) mixtures at high pressures.

#### **Outreach Activities:**

Research findings were presented at the AIChE and ACS National meetings, and were published in technical journals and proceedings.

**Journal Publications**

E. Kiran, H.Pohler, Y. Xiong, "Volumetric properties of pentane + carbon dioxide at high pressures", Journal of Chemical & Engineering Data, p. 158, vol. 41, (1996). Published

H. Pohler, E. Kiran, "Volumetric properties of carbon dioxide + toluene at high pressures", Journal of Chemical & Engineering Data, p. 482, vol. 41, (1966). Published

Z. Gokmenoglu, Y. Xiong, E. Kiran, "Volumetric properties of carbon dioxide + sulfur hexafluoride at high pressures", Journal of Chemical & Engineering Data, p. 354, vol. 41, (1966). Published

H. Pohler, E. Kiran, "Volumetric properties of sulfur hexafluoride + pentane and sulfur hexafluoride + toluene at high pressures", Journal of Chemical & Engineering Data, p. 389, vol. 42, (1997). Published

E. Kiran, Z. Gokmenoglu, "Density modulated supercritical levitation polymerization", ACS Polymer Materials Science and Engineering, p. 406, vol. 74, (1966). Published

**Books or Other One-time Publications****Web/Internet Site****Other Specific Products****Contributions****Contributions within Discipline:**

The finding of this research especially the data base generated on volumetric properties of binary fluid mixtures and their densities have been far reaching. In addition to providing basic thermodynamic information, the data have been of value to those working on not only polymerization, but a wider range of applications in processing of natural or synthetic polymers, pharmaceutical compounds, and inorganic materials. The concept of levitation with supercritical fluids is still novel and is expected to be explored for new applications pertaining to morphological changes in polymer materials in the future.

**Contributions to Other Disciplines:**

The data base generated is of value to those working in pharmaceuticals, inorganic materials processing, natural materials, and those working on modeling and simulations of complex multi-component systems.

**Contributions to Human Resource Development:**

The project contributed to the educational experience of two graduate students and a postdoctoral fellow.

**Contributions to Resources for Research and Education:**

The funds through this exploratory research project were very modest, and did not provide contributions to enhancement of the laboratory infrastructure through purchase of any new research equipment. However, the fundamental data that has been generated on binary fluid mixtures has been of great value for other research activities that have been conducted, one example being the potential use of binary fluid mixtures as solvent and carrier medium in impregnation and as pressure-sensitive nonsolvent to bring achieve pressure-induced in-situ precipitation of functional chemicals or polymeric materials in complex networks such as wood.

**Contributions Beyond Science and Engineering:****Categories for which nothing is reported:**

Organizational Partners

Any Book

Any Web/Internet Site

Any Product

Contributions: To Any Beyond Science and Engineering

***NSF Grant 9310232  
Supercritical Levitation Polymerization and Processing  
Final Report (October 29, 1996)***

In supercritical polymerization processes, in the absence of special additives such as surfactants, polymer chains grow to molecular weights determined by their solubility under the prevailing conditions (temperature/pressure) of the solvent. Further growth in the chain length results in phase separation, and normally leads to precipitation. The objective of this project was to conduct polymerization under density matched (isopycnic) conditions by adjusting the density of the polymerization medium to be identical to the density of the polymer formed. This iso-density operation was expected to insure levitation by buoyancy and prevent (or delay) precipitation of the phase-separated polymer and promote formation of higher molecular weights and controlled morphologies. This would be a unique way of simulating the microgravity environment of space-based processes on earth. Since density adjustments are readily achievable for supercritical fluids through manipulation of either the pressure or the temperature, the technique would be of wide utility in other isopycnic processes.

Research was conducted along two parallel paths. The results are summarized below:

(I) One activity area was to generate an experimental data base on the density of fluid mixtures which can span a wide range of values with changes in pressure and temperature. Densities of carbon dioxide, pentane, toluene, and sulfur hexafluoride as pure fluids, and the densities of binary mixtures “carbon dioxide + pentane”, “carbon dioxide + toluene”, “carbon dioxide + sulfur hexafluoride”, “pentane + sulfur hexafluoride” and toluene + sulfur hexafluoride” were determined in the temperature range from 323 to 423 K at pressures up to 70 MPa for a wide range of compositions for each mixture. Depending upon the fluid system, conditions to achieve fluid densities in the range from about 0.6 to 1.6 gcm<sup>-3</sup> have been documented. The results have been published in the Journal of Chemical Engineering Data (See attached list of publications and presentations). The work has been further extended, and we recently completed the mapping the density for a number of other binary mixtures such as carbon dioxide + acetone and carbon dioxide + ethanol.

(II) The second area of activity was to conduct free-radical polymerization of styrene in these binary mixtures. The polymerization in binary mixtures of carbon dioxide plus another solvent is by itself of interest since this methodology can be extended to many processing situations to reduce, or replace the conventional solvents. In “carbon dioxide + pentane”, and “carbon dioxide + toluene” mixtures, maximum densities achievable are limited by the density of carbon dioxide and were below 1.0 gcm<sup>-3</sup> at pressures up to 70 MPa. Densities greater than 1.0 were accessible in mixture containing sulfur hexafluoride. In any given fluid mixture, increasing the polymerization pressure resulted in formation of higher molecular weight polymer due to increased demixing thresholds. Compared to carbon dioxide, increasingly higher molecular weight polymers were produced in going from pentane to toluene and to sulfur hexafluoride. In carbon dioxide

+ sulfur hexafluoride mixtures, polymerizations conducted in the density range in the vicinity of  $1.05 \text{ gcm}^{-3}$  resulted in dramatic increases in the molecular weight of the polymer formed. Since the density of polystyrene is about 1.05, this dramatic increase was indeed a result of levitation of the polymer formed. These findings were presented at the AIChE Annual Meetings in 1994 (San Francisco) and 1995 (Miami Beach), and the ACS National Meeting in New Orleans in March 1966, and have been published in the ACS PMSE Preprints. (See attached list of publications and presentations).

As described this project has been very successful not only in demonstrating the concept but also in generating the extensive data base for much broader utility. We are now extending the data base and the concept of levitation to other areas such as particle formation from supercritical fluids and other phase separation processes.

We are grateful to NSF for providing the funds for this exciting and innovative project. Considering the modest funding level (a total of \$50,000) for this exploratory project, we feel we have accomplished a lot.

### **Publications and Presentations based on Research funded by NSF Grant CTS 9310232**

#### **Publications**

1. E. Kiran, H. Pöhler and Y. Xiong, "Volumetric properties of pentane + carbon dioxide at high pressures", *J. Chem. Eng. Data*, 41, 158-165 (1996).
2. H. Pöhler and E. Kiran, "Volumetric properties of carbon dioxide + toluene at high pressures", *J. Chem. Eng. Data*, 41, 482-486 (1996).
3. Z. Gokmenoglu, Y. Xiong and E. Kiran, "Volumetric properties of carbon dioxide + sulfur hexafluoride at high pressures", *J. Chem. Eng. Data*, 41, 354-360 (1996).
4. H. Pöhler and E. Kiran, "Volumetric properties of sulfur hexafluoride + pentane and sulfur hexafluoride + toluene at high pressures", *J. Chem. Eng. Data*, accepted for publication.
5. E. Kiran and Z. Gokmenoglu, "Density modulated supercritical levitation polymerization", *Proc. ACS Polym. Materials Sci. & Eng.*, 74, 406-407 (1966).

#### **Presentations**

1. E. Kiran and Z. Gokmenoglu, Polymerization of styrene in supercritical fluids, Presented at the AIChE 1994 Annual meeting, San Francisco, CA, November 13-18, 1994. Abstract 121f.
2. E. Kiran and Z. Gokmenoglu, Density modulated polymerization in supercritical fluids, Presented at the AIChE 1995 Annual meeting, Miami Beach, FL November 12-17, 1995; Abstract 73g.
3. Y. Xiong, H. Pöhler, Z. Gokmenoglu and E. Kiran, PVT behavior of binary supercritical fluid mixtures. Carbon dioxide – sulfur hexafluoride, carbon dioxide

- pentane, and carbon dioxide –toluene mixtures, Presented at the AIChE 1995 Annual meeting, Miami Beach FL, November 12-17, 1995; Abstract 33h.
4. E. Kiran and Z. Gokmenoglu, Density modulated supercritical levitation polymerization, Presented at the 211<sup>th</sup> ACS National meeting, New Orleans, LA March 24-28, 1966; Paper 241.