Edited by
Maartje F. Kemmere, Thierry Meyer

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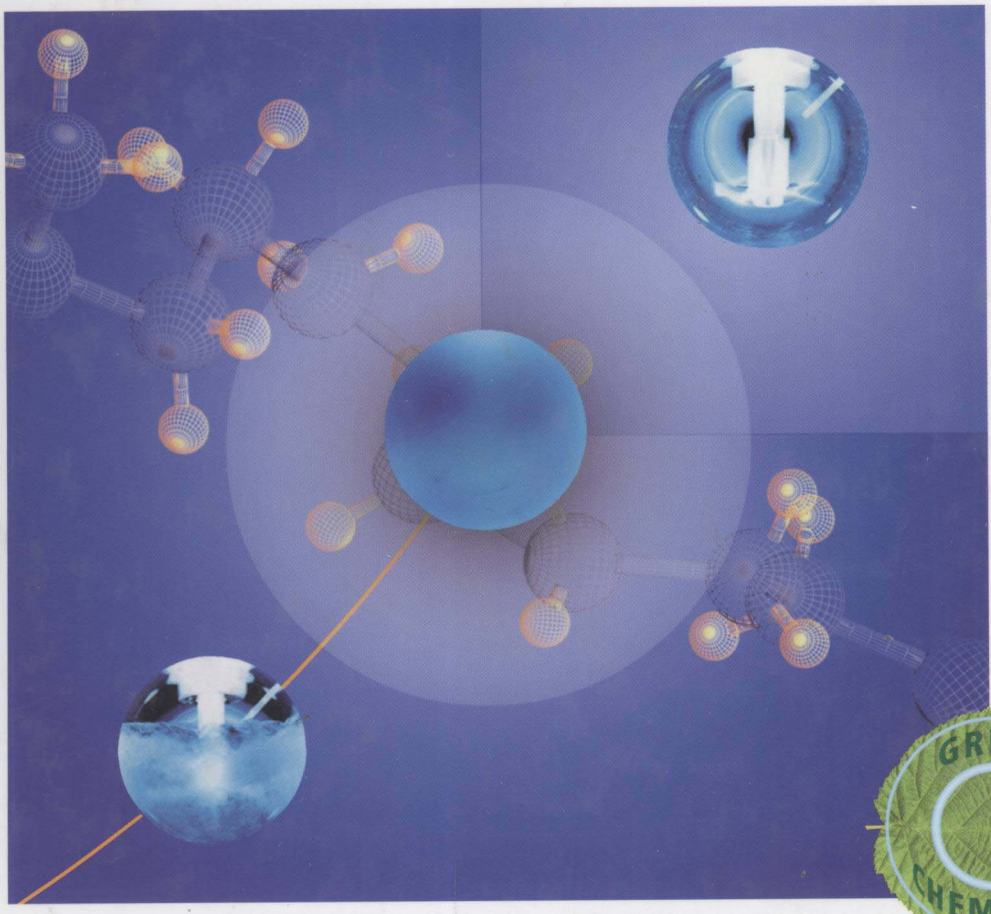
Supercritical Carbon Dioxide

in Polymer Reaction Engineering



GREEN CHEMISTRY

Supercritical Carbon Dioxide

in Polymer Reaction Engineering

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Maartje F. Kemmere and Thierry Meyer

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Supercritical Carbon Dioxide

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Foreword

Supercritical fluid technology encompasses a very broad field, which includes various reaction, separation, and material formation processes that utilize a fluid at a temperature greater than its critical temperature and a pressure greater than its critical pressure. Supercritical fluids generally are compressed gases, which combine properties of gases and liquids in a chemically interesting manner. Supercritical fluids have physicochemical properties in between a liquid and a gas. They can have a liquid-like density and no surface tension while interacting with solid surfaces. They can have gas-like low viscosity and high diffusivity and, like a liquid, can easily dissolve many chemicals and polymers.

When Professor Thomas Andrews reported the measurement of the critical properties of carbon dioxide as part of his 1876 Bakerian Lecture "On the Gaseous State of Matter", he probably could not have envisaged that this important industrial gas would also become very popular in supercritical fluid technology. In fact carbon dioxide's popularity stems from the fact that it is nontoxic and nonflammable, it has a near ambient critical temperature of 31.1 °C, and that it is the second least expensive solvent after water. The most widespread use of supercritical carbon dioxide has been in Supercritical Fluid Extraction processes for the food and pharmaceutical industries with several large extraction units in operation in the United States and in Europe for decaffeinating coffee and tea and extracting flavors and essential oils from hops, spices, and herbs. Other applications have been reported in recrystallization of pharmaceuticals, purification of surfactants, cleaning and degreasing of products in the fabrication of printed circuit boards, and as a substitute for organic diluents in spray painting and coating processes.

The potential of supercritical carbon dioxide in polymer processes has been recently a focus of research and development both in academia and in industry. The main driver behind this effort is the chemical industry's pursuit of sustainable growth strategies, which aim to reduce the environmental footprint of existing or new polymer processes. The objective of the research and development effort has been to demonstrate whether carbon dioxide can be applied as an environmentally friendly substitute for many halogenated and other organic solvents used in polymer processes thereby reducing atmospheric pollution and eliminating solvent residues in products. Supercritical carbon dioxide could be most advantageously applied in developing improved polymer processes and

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products when environmental compliance pressures would require a process change, when regulatory requirements could require changes in product purity, and when improved products in terms of performance can result from substituting the traditional solvent with carbon dioxide.

This book edited by Professors M. Kemmere and Th. Meyer provides both academic researchers and industrial practitioners a thorough overview of the state of the art of the application of supercritical carbon dioxide in polymer processes by carefully balancing the exposition of recent research results and emerging commercial applications with the discussion of the special challenges and needs of this exciting new technology. Written mainly by prominent American and European academic researchers in the field, the book is comprised of three parts, which focus on the fundamentals aspects of this technology (thermodynamics, transport phenomena, and polymerization kinetics), and its application in polymerization reactions (including dispersion and emulsion systems as well as fluoropolymers synthesis) and polymer processing operations (including extrusion and reduction of residual monomer).

We hope that the publication of this book, which will surely become a standard reference in the field, will spur the interest in further exploring the potential of supercritical carbon dioxide applications in polymer technology both in terms of fundamental understanding of the relevant physico-chemical phenomena and in advancing the state of the design and commercialization of environmentally friendly polymer processes producing products with unique performance characteristics.

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Preface

The idea of producing a book on the application of supercritical carbon dioxide in polymer processes was born on a fine November evening in Barcelona during the meeting of the European Working Party on Polymer Reaction Engineering in 2002. As the idea still seemed reasonable the next morning, we decided to put words into action, and two years later the book was complete. From the outset, we were determined to give the manuscript a chemical engineering focus because of the increasing number of supercritical polymer processes on the verge of industrial application.

Our aim has been to present a state-of-the-art overview of polymer processes in high-pressure carbon dioxide using a multidisciplinary and synergetic approach that starts from fundamentals, goes through polymerization processes, and ends with post-processing. The contributors to this book are internationally recognized experts from different fields of CO_2-based polymer processes from Europe and the United States. We would like to express our gratitude to all the authors for the high quality of every contribution, and we are convinced that this compilation will become a reference book in the field.

Editing a book has resulted in strong links between Eindhoven and Lausanne, enabling us to adopt the good habits of both countries. In particular, the happy evenings spent with Francine, Jos, Morgane, and Quentin were a real pleasure, not only due to the presence of "tarte à la crème", "stroopwafels", "crème brulée", and too many chocolates, but also by the sealing of a strong friendship. This home support and understanding, also when we were traveling, certainly facilitated the editing process by introducing fun and fresh air into a hard job.

Furthermore, many thanks are due to our collaborators in the Process Development Group in Eindhoven and the Polymer Reaction Engineering Group in Lausanne for their creativeness and enthusiasm in the field of polymer science in supercritical carbon dioxide. Finally, we would like to thank Karin Sora and her team from Wiley-VCH for their great help in producing this book.

Eindhoven and Lausanne, July 2005

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