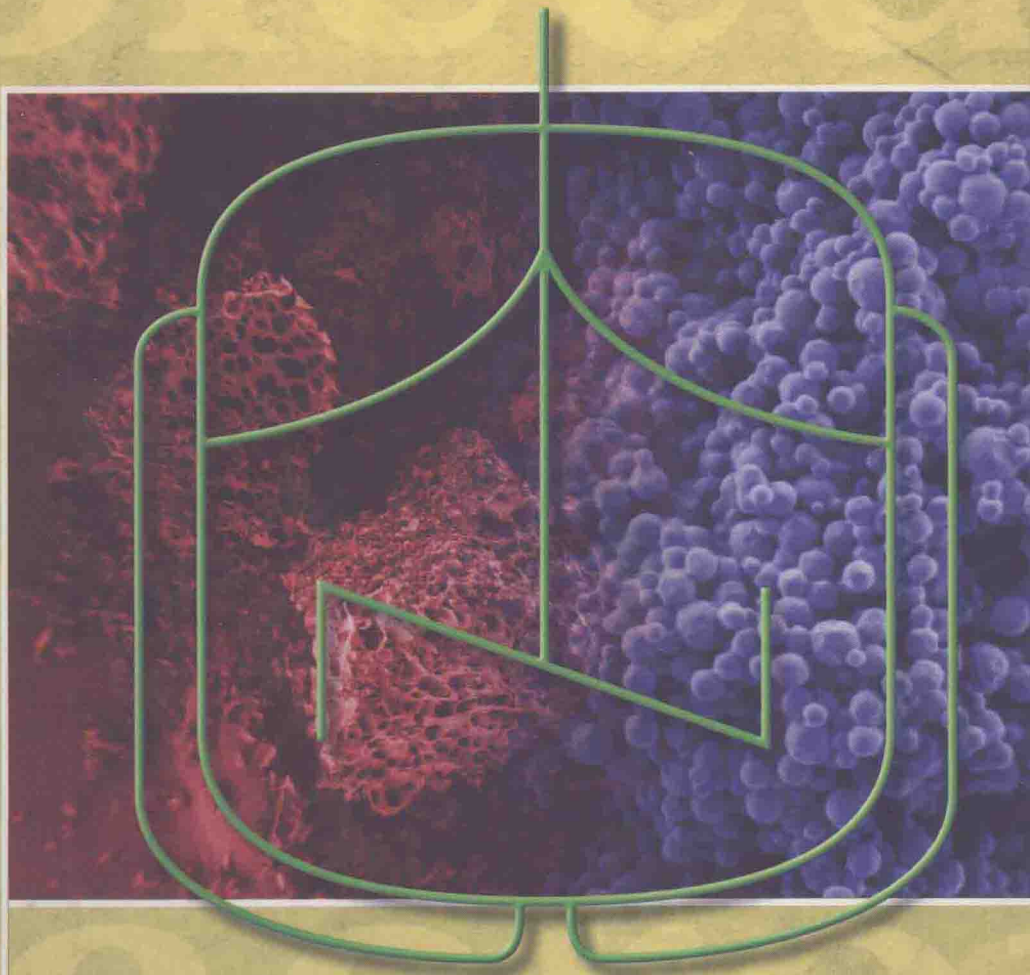
Macromolecular Symposia 259

H.-U. Moritz, W. Pauer (Eds.)

Polymer Reaction Engineering –

9th International Workshop



WILEY-VCH

Macromolecular Symposia Vol. 259

Polymer Reaction Engineering - 9th International Workshop

Selected Contributions
from the conference at the
University of Hamburg (Germany)
October 7–10, 2007

Symposium Editors:
Hans-Ulrich Moritz, Werner Pauer
(University of Hamburg, Germany)

WILEY-VCH

UHH
Universität Hamburg

Full text and further information: www.ms-journal.de

Macromolecular Symposia
is published 14 times a year

Annual subscription rates 2008
Macromolecular Full Package
(All seven *Macromolecular Journals*; 101 issues in total):

Europe	Euro	8,999	9,899
Switzerland	Sfr	14,995	16,495
All other areas	US$	11,895	13,085
		print only **or** electronic only	print **and** electronic

Postage and handling charges included.
All Wiley-VCH prices are exclusive of VAT.
Prices are subject to change.
Individual subscriptions, single issues and back copies are available.
Please ask for details at: service@wiley-vch.de

Orders may be placed through your bookseller or directly at the publishers:
WILEY-VCH Verlag GmbH & Co. KGaA,
P.O. Box 10 11 61, 69451 Weinheim, Germany,
Tel. +49 (0) 62 01/6 06-400,
Fax +49 (0) 62 01/60 61 84,
E-mail: service@wiley-vch.de

Copyright Permission:
Fax: +49 (0) 62 01/6 06-332,
E-mail: rights@wiley-vch.de

For USA and Canada: Macromolecular Symposia (ISSN 1022-1360) is published with 14 volumes per year by WILEY-VCH Verlag GmbH & Co. KGaA, Boschstr. 12, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003, USA. Application to mail at Periodicals Postage rate is pending at Jamaica, NY 11431, USA. POSTMASTER please send address changes to: Macromolecular Symposia, c/o Wiley-VCH, 111 River Street, Hoboken, NJ 07030, USA.

Printed on acid-free paper.
Typesetting: Thomson Digital (India) Ltd., India
Printing: Strauss Offsetdruck, Mörlenbach
Binding: Litges & Dopf, Heppenheim

Macromolecular Symposia | 259

Polymer Reaction Engineering -
9th International Workshop

Selected Contributions
from the conference at the
University of Hamburg (Germany)
October 7–10, 2007

Symposium Editors:
Hans-Ulrich Moritz, Werner Pauer
(University of Hamburg, Germany)

Matyjaszewski, K., Gnanou, Y.,
Leibler, L. (Eds.)

Macromolecular Engineering
Precise Synthesis,
Materials Properties, Applications
2007, Hardcover
ISBN: 978-3-527-31446-1

Meyer, T., Keurentjes, J. (Eds.)

Handbook of Polymer
Reaction Engineering
2005, Hardcover
ISBN: 978-3-527-31014-2

Wilks, E. S. (Ed.)

Industrial Polymers Handbook
Products, Processes, Applications
2001, Hardcover
ISBN: 978-3-527-30260-4

M. Hess (Ed.)

Polychar-15
World Forum on Advanced Materials
Vol. 258

J.B.P. Soares (ed.)

Polyolefin Characterization
Vol. 257
ISBN: 978-3-527-32192-6

This volume represents the proceedings of the 9th International Workshop on "Polymer Reaction Engineering" held at the University of Hamburg, Germany, in cooperation with DECHEMA (Gesellschaft für Chemische Technik und Biotechnologie e.V., Frankfurt a. M.), October 7–10, 2007.

For more than twenty years the workshop series and the corresponding proceedings successfully accompany the chemical community promoting the update, exchange and discussion of new findings in the field of polymer reaction engineering between experts from academia and industry alike. With almost 200 participants the 9th International Workshop was one of the largest meetings of this kind worldwide. As long as this workshop exists the organizers fund young scientists to take part in the conference. This year 30 % of the participants were young PhD students, and thanks to the generous support of WILEY-VCH Publisher, awards for the two most outstanding poster presentations could be granted.

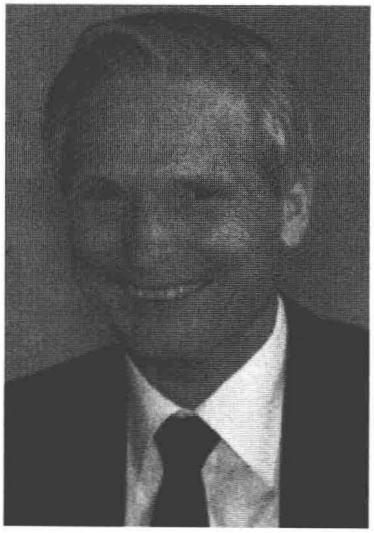
After all, 35 % participants from industry document special relevance attached to the conference. From 70 accepted contributions almost 75 % are compiled in the present proceedings. Excellent papers of emerging new concepts and promising developments, technologies from neighboring fields of chemical engineering and industrial solutions in process and product design are widely discussed from a superior perspective. New catalysts and catalytic polymerization processes, controlled radical polymerization, high-throughput and micro technologies, new reactor and process design and intensified processes are included. Polymer thermodynamics, process analytics, modeling and process control enable development and application of these technologies. Distinctive spotlights were put on contributions of new environmentally benign polymerization processes in consideration of economical needs. Furthermore nanotechnologies perform new and extended characteristics to polymer materials.

We thank all the contributors for providing their manuscripts and thankfully acknowledge WILEY-VCH Publisher for publishing this volume, thus making the proceedings available forthwith to the meeting not only to the conference attendees.

We are deeply grateful to DECHEMA for organizing this workshop as an outstanding international conference and especially encouraging young scientists to join the scientific community.

Finally we like to thank the members of the Scientific Advisory Committee for helping to establish a scientific program of high quality and for careful revision of the contributions.

H.-U. Moritz, W. Pauer



Heinz Gerrens

September 1st, 1923, Hamburg – May, 14th, 2007, Frankenthal

Prof. Dr. Heinz Gerrens started his career as student of Günter Victor Schulz at the Institute of Physical Chemistry at the Johannes Gutenberg University in Mainz, Germany, where a large variety of topics were covered, among them the kinetics of polymerization at high conversion, transfer reactions and their importance for branched polymers and new methods for the determination of molecular weight distribution and the size as well as the shape of macromolecules and their properties in solution.

After joining BASF **Heinz Gerrens** put his main interests in the influences of reactor type and operation on polymer properties and semibatch as well as continuous emulsion polymerization, thus becoming one of the founders of modern Polymer Reaction Engineering. He published numerous brilliant reviews especially in the 1960's and 70's, however the most distinguished in *Ullmann's Encyclopedia of Industrial Chemistry*. As honorary professor of the University of Karlsruhe he always kept engaged in the education of young scientists for decades, which he believed to be essential for future common welfare. In this context his contribution to *Fitzer, Fritz: Technische Chemie - Einführung in die Chemische Reaktionstechnik* is recognized as fundamental. With emphasis and determination he helped to establish the DECHEMA course of Polymer Reaction Engineering for advanced training of industrial chemists and engineers in which he acted as a lecturer for more than fifteen years, despite a feeble health even after his retirement in 1982. Finally, it was up to **Heinz Gerrens** to speak the closing remarks of the International Workshop of Polymer Reaction Engineering as long as he was able to take an active part, not only presenting statistics, but always trying to find an outlook for future trends and developments. The scientific community of Polymer Reaction Engineering owes deep gratitude to his great personality.

His colleagues, collaborators and students will remember him as an exceeding, competent and inspiring counterpart. Even though he felt a great affinity to the mountains, especially to the Alps, he stayed a "hanseatic" in its best sense: a person of cordial integrity, liberal, open-minded, dignified, but disciplined to himself.

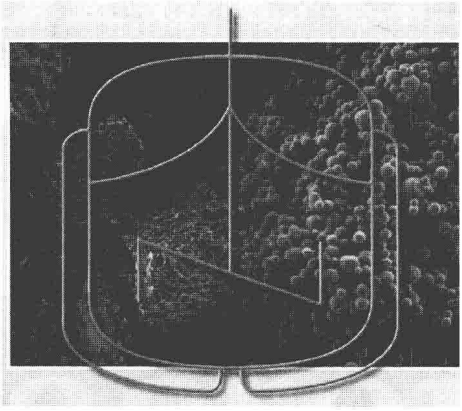
Macromolecular Symposia: Vol. 259

Articles published on the web will appear several weeks before the print edition. They are available through:

WILEY InterScience®

www.interscience.wiley.com

Cover: The picture on the cover is based on the article by M. Morbidelli et al. (p. 218), and shows SEM photographs of PMMA samples.



Polymer Reaction Engineering -

9th International Workshop

University of Hamburg (Germany)

Dedicated to Prof. Heinz Gerrens

DOI: 10.1002/masy.200751301

Miniemulsification: An Analysis of the Use of Rotor Stators as Emulsification Devices

Ula El-Jaby,[1,2] *Timothy F. L. McKenna,*[*1,2] *Michael F. Cunningham*[1]

Summary: Production of polymeric latexes by miniemulsion techniques is clearly attracting more and more attention for a number of reasons. However, one of the limiting factors in the acceptance of miniemulsion polymerisation as a commercialisible technique was that in early laboratory studies ultrasonication was the only method considered for the generation of polymerisable droplets. It is shown in the current paper that rotor stator mixers are an promising alternative. In addition to demonstrating the feasibility of these techniques, an investigation of the evolution of the particle size distribution during polymerisation revealed that controlled coalescence can occur for reasons that are difficult to identify.

Keywords: emulsification; miniemulsion polymerisation; rotor stator mixers; static mixers; tubular reactors

Introduction

The production of polymers via free radical polymerisation in colloidal dispersions continues to be of economic significance for a number of reasons including: a desire to substitute current solvent-based systems with an aqueous medium for environmental reasons; a reduction in the bulk viscosity of the reactor contents (better heat transfer, easier handling); and the ease of manipulation of sticky or film forming materials. Traditionally a large majority of such products have been made by suspension and conventional emulsion polymerisation.

More recently, the ease with which one can incorporate a wide range of organic and inorganic materials into the final product, as well as the ability to directly produce and emulsify dispersions with solids contents of up to 50 or even 60 volume per cent[1] have made miniemulsions more and more attractive as an alternative means for production of heterogeneous aqueous dispersions of polymer particles.[2]

Miniemulsion droplets, with diameters typically on the order of 100–500 nm, are created by mechanically dispersing an organic phase in an aqueous medium. The key components contributing to the stability of the miniemulsion droplets are the surfactant which prevents coalescence and the co-stabiliser which reduces the rate of Ostwald ripening.[3] When the polymerisation proceeds via a free radical mechanism, nucleation takes place in the monomer droplet. Thus either water-soluble, or oil soluble initiator can be used.[4–6]

The dispersion of the droplets, and to a large extent the size of the polymerisable mini-emulsion droplets will be determined by the chemical components of the stabilisation system, the nature of the monomer(s) being emulsified (hydrophobic monomers will form larger droplets than hydrophilic ones all other things being equal), and most importantly the type of mechanical deviceused for the emulsification step.[7] Various homogenization devices can be used, with the most common at the laboratory scale being ultrasonic probes. However such devices are, on the whole, not practical at

[1] Department of Chemical Engineering, Queen's University, Kingston, ON, Canada
E-mail: tim.mckenna@chee.queensu.ca
[2] LCPP – CNRS/ESCPE Lyon, 43 Bd du 11 Novembre 1918, 69616 Villeurbanne, France

the industrial scale. Other methods include high pressure homogenizers,[2] static mixers,[8] or rotor-stator mixers.[8,9] All of these devices are of interest at the current time since they have been widely used in other areas of agri- and petrochemical processes. It is clear that they can be economically viable, safely used and can be extrapolated for use on a large scale (not the case with ultrasound).

Earlier studies from other groups have shown that high pressure homogenisers are a credible alternative to ultrasound for the generation of dispersions,[2] thus we will not pursue this farther here, but rather will explore other alternatives to this route. Recent work by Ouzineb et al. investigated the use of the rotor-stator mixer, as well as in-line mixers to make miniemulsion droplets (300–800 nm) using styrene or butyl methacrylate as monomers with a solid content of 47.5%, sodium dodecyl sulphate (SDS) and Triton 405-X as emulsifiers, and stearyl methacryate (SMA) as a reactive co-stabiliser.[8] This work focused on different single monomer systems with similar levels of hydrophobicity, however the authors did not discuss polymerisations but focused only on the creation of the dispersions. In previous studies, Cunningham et al. used a high shear rotor-stator for the creation of microsuspension droplets (2–400 microns) of MMA containing AIBN, BPO and LPO as initiators and PVOH as the stabilising system.[9] Experimental methods consisted of mixing the pre-emulsified mixture for 4 minutes at 5000 rpm to make droplets of 10 μm, and 2 minutes at 15 000 rpm to make droplets of 2 μm. However these droplets are too small to be of practical use in the applications (e.g. coatings) that we are looking at here. The objective of the current paper is to present preliminary results obtained during the investigation of the use of a rotor-stator mixer for the production of mixtures of monomers with different hydrophocities (MMA plus BA), and to attempt to understand the role of the different process parameters in the evolution of the PSD during the reaction. Parallel work is being carried out on static mixers as a means of generating miniemulsions. A future paper from this research group will show these results and compare the different means of making miniemulsions.

Experimental Part

All compounds used in this study were used as received from the suppliers. The monomers were methyl methacrylate (MMA) and butyl acrylate (BA) were used as received. The surfactant used was sodium dodecylbenzene sulfate (SDBS) (Acros 88% technical grade) and Disponil® A 3065 (Cognis – 37%). The co-stabilisers tested were octadecyl acrylate (ODA) (Aldrich, 97%) and n-hexadecane (HD) (Acros, 99%). The oil soluble initiators used were dilauryl peroxide (LPO) (Acros, 99%), dibenzoyl peroxide (BPO) (Acros, 75%), and 2,2′-azobis(2-methylpropionitrile) (AIBN) (Acros, 98%).

Miniemulsions were made using a 50:50 w/w mixtures of the two monomers with solid contents ranging from 47–55% weight percent. The organic phase contained 10 wt% co-stabiliser, 0.4–1.2 wt% of surfactant, and 0.14 wt% of initiator based on total monomer mass. Prior to emulsification, the monomers, co-stablisers and (eventually) oil soluble initiators were mixed together under gentle agitation at room temperature, and the surfactants were dissolved in the deionised water and prepared as a second phase. The two phases were then combined and subjected to high shear using the rotor – stator mixer. The miniemulsion droplets were made using a Turbotest® rotor - stator (RAYNERI) having a maximal rotation rate of 3300 rpm. The rotor stator assembly was a H30 Form B and a 5.5 cm interior diameter stator was used with a four blade rotor. The stator head has 19 vertical slits along the side and 12 circular slots along the top. The solutions to be emulsified were introduced into a 1 litre jacketed glass reactor containing a hexagonal baffle-like insert to reduce the vortex. This configuration was preferable to standard baffle configurations since the lack of sharp angles reduced

