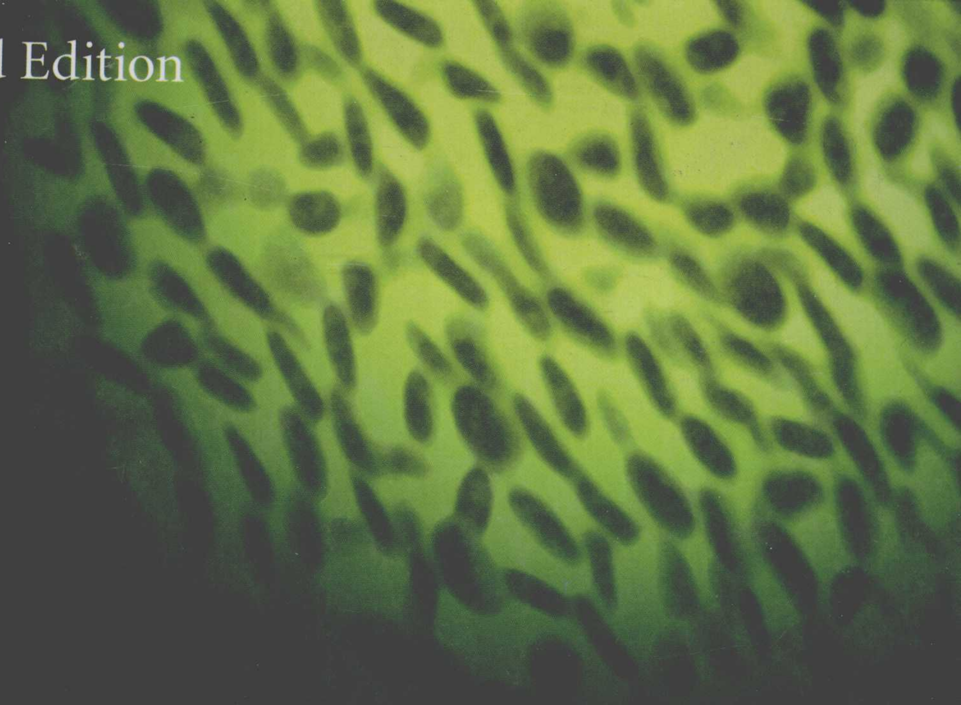

Second Edition

Chemistry and Technology of Emulsion Polymerisation

Editor A. M. van Herk

WILEY

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This edition first published 2013

Registered office
John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, United Kingdom

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Library of Congress Cataloging-in-Publication Data applied for.

A catalogue record for this book is available from the British Library.

ISBN: 9781119953722

Set in 10/12pt Times by Aptara Inc., New Delhi, India.
Printed and bound in Malaysia by Vivar Printing Sdn Bhd

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Abbreviations

AA	Acrylic acid
ABS	Acrylonitrile-butadiene-styrene
Aerosol MA	AMA, sodium di-hexyl sulfosuccinate
Aerosol OT	AOT, sodium di(2-ethylhexyl)sulfosuccinate
AFM	Atomic force microscopy
AIBN	Azobisisobutyronitrile
ATRP	Atom transfer radical polymerization
B	Butadiene
BA	n-Butyl acrylate
BPO	Benzoyl peroxyde
Buna N	Butadiene-acrylonitrile copolymer
Buna S	Butadiene-styrene copolymer
CCA	Colloidal crystalline array
CCD	Chemical composition distribution
CDB	Cumyl dithiobenzoate
CFM	Chemical force microscopy
CFT	Critical flocculation temperature
CMC	Critical Micelle Concentration
CMMD	Control molar mass distribution
CPVC	Critical pigment volume concentration
CRP	Controlled radical polymerization techniques
CTA	Chain transfer agents
CVP	Colloid vibration potential
Cyclam	Tetrazacyclotetradecane
DLVO	Derjaguin-Landau-Verwey-Overbeek
DMA	Dynamic mechanical analysis
DNA	Desoxy nucleic acid
DSC	Differential scanning calorimetry
EDTA	Ethylene diamino tetraacetic acid
EHMA	2-Ethylhexyl methacrylate
EPA	Environmental Protection Agency
ESA	Electrokinetic sonic amplitude
ESEM	Environmental scanning electron microscopy
FESEM	Field emission scanning electron microscopy
FIB-SEM	focused ion beam SEM

FFF	Field-flow fractionation
FLGN	Feeney, Lichti, Gilbert and Napper
HASE	Hydrophobically modified alkali-swellable emulsions
HDPE	High density polyethylene
HEC	Hydroxy ethyl cellulose
HEMA	2-Hydroxyethyl methacrylate
HEUR	Hydrophobically modified ethylene oxide urethanes
HIC	Hydrophobic interaction chromatography
HPLC	High performance liquid chromatography
HUFT	Hansen, Ugelstad, Fitch, and Tsai
IR	Infrared
K	Kelvin
LV-SEM	low voltage SEM
LRP	Living radical polymerisation
MA	Methyl acrylate
MFFT	Minimum film forming temperature
MMA	Methyl methacrylate
MMD	Molar Mass Distribution
MONAMS A5	1-(methoxycarbonyl)eth-1-yl initiating radical
NMP	Nitroxide-mediated living radical polymerisation
NMR	Nuclear magnetic resonance
NR	Natural rubber
OEM	Original Equipment Manufacturer
OM	Optical microscopy
PCH	Phenyl-cyclohexene
PCS	Photon correlation spectroscopy
PDI	Polydispersity index
PDMS	Poly(dimethylsiloxane)
PEO	Poly(ethylene oxide)
PGA	Poly(glycolic acid)
PHS	Poly(hydroxystearic acid)
PLA	Poly(D, L-lactic acid)
PLGA	Poly(glycolic-co-lactic acid)
PMMA	Poly(methylmethacrylate)
PNIPAM	Poly(N-isopropylacrylamide)
PPO	Polypropylene oxide
PRE	Persistent radical effect
PSA	Pressure sensitive adhesives
PSD	Particle size distribution
PTA	Phosphotungstic acid
PTFE	Poly tetrafluorethylene
PVAc	Poly(vinyl acetate)
PVC	Pigment volume concentration
QCM-D	quartz crystal micro-balance with dissipation monitoring
RAFT	Reversible addition fragmentation transfer
RCTA	Reversible chain transfer agents

S	Styrene
SAM	Self-assembled monolayer
SANS	Small angle neutron scattering
SAXS	Small angle X-ray scattering
SB	Styrene butadiene
SBLC	Styrene butadiene latex council
SBR	Styrene butadiene rubber
SDS	Sodium dodecyl sulphate
Sed-FFF	Sedimentation field-flow fractionation
SEM	Scanning electron microscopy
SFM	Scanning force microscopy
SPM	Scanning probe microscopy
SRNI	Simultaneous reverse and normal initiation
SSIMS	Static secondary ion mass spectrometry
STM	Scanning tunneling microscopy
TEM	Transmission electron microscopy
TEMPO	2,2,6,6-Tetramethylpiperidine-l-oxyl
Texanol®[c]	2,2,4-Trimethyl-1,3-pentanediol-diisobutyrat
UAc	Uranyl acetate
UV	Ultraviolet
Vac	Vinyl acetate
VCH	Vinyl-cyclohexene
VOC	Volatile organic compound
W	Watt
Wet-SEM	wet scanning transmission electron microscopy
XPS	X-ray photoelectron spectroscopy
XSB	Carbo**x**ylated **s**tyrene-**b**utadiene dispersions

List of Frequently Used Symbols

a_e	Specific surface area for a emulsifier molecule on a polymeric surface
A	Arrhenius constant of the initiation (A_i), propagation (A_p), termination (A_t) and transfer (A_{tr})
$\bar{d}$	average particle diameter d_n, number average diameter, d_s surface average diameter, d_w weight average diameter, d_v volume average diameter
d_w/d_n	particle diameter non-uniformity factor
E	energy of activation for initiation (E_i), propagation (E_p), termination (E_t) and transfer (E_{tr})
f	Initiator efficiency
F	Efficiency factor for adsorption
ΔG	Partial molar free energy of droplets ΔG_d, ΔG_a of the aqueous phase and of the latex particles ΔG_l
H	enthalpy
ΔH	change in enthalpy
j_{crit}	Critical length of an oligomer at which precipitation from the aqueous phase occurs
k	exit frequency
k	rate constant of the initiation (k_i), propagation (k_p), termination (k_t) and transfer reaction (k_{tr})
[M]	concentration of monomer, $[M]_p$ concentration of monomer in the polymer particles. If this depends on quantities such as radius r, time t, etc., the recommended notation is $[M(r,t,\ldots)]_p$. $[M]_a$ for the monomer concentration in the aqueous phase, $[M]_{a,sat}$ for the saturation concentration in the aqueous phase.
M	average molar mass: number-average molar mass (M_n). weight-average molar mass (M_w),
N	number of latex particles per unit volume of latex
N_n	Number of particles with n radicals per particle
N_A	Avogadro constant
n	number of radicals in a latex particle
$\bar{n}$	average number of radicals per particle
n_{m0}	initially added number of moles of monomer per unit volume
$\overline{P}_n$	number average degree of polymerisation
R	gas constant
$r_{1,2}$	reactivity parameters in copolymerisation
r_p	rate of polymerisation per particle

r_e	rate of entry of radicals per particle
r_t	rate of termination per particle
r_o	the radius of the unswollen micelles, vesicles and/or latex particles.
R_p	Rate of polymerisation
S	entropy
ΔS	change in Entropy
T	temperature
T_g	glass transition temperature
t	time
V	volume of monomer swollen latex particles
V_m	molar volume of the monomer
v_p	volume fraction of polymer
W	stability ratio
w_p	mass fraction of polymer in the particle phase
x	fraction conversion of monomer to polymer
x_n	number-average degree of polymerisation, x_w weight-average degree of polymerisation
z-mer	The length of an oligomer in the aqueous phase at which surface activity occurs
α	fate parameter (fate of excited radicals)
χ	Flory-Huggins interaction parameter
δ	solubility parameter or chemical shift
ε	permittivity
γ	interfacial tension
η	viscosity
$[\eta]$	intrinsic viscosity
ν	kinetic chain length
π	osmotic pressure
ρ	entry frequency
ρ_i	radical flux or rate of initiation (2 kd f [I])
μ	Volume growth factor
τ_g	time of growth of a polymer chain

Introduction to the Second Edition

The increasing need for environmentally benign production methods for polymers has resulted in a further development and implementation of the emulsion polymerisation technique. More and more companies switch from solvent based polymer production methods to emulsion polymerisation.

Since the introduction of the first edition in 2005 the experience gained with using this book in a teaching environment, led us to this second improved edition. Besides some of the new developments we added a new chapter on latex particle morphology development as especially in this area much progress has been made and a lot of research efforts, both in academia and in industry, has been devoted to this important area. Furthermore the chapter on the use of controlled radical polymerization in latex production has been substantially updated as most of the other chapters.

Powerpoint slides of figures in this book for teaching purposes can be downloaded from http://booksupport.wiley.com by entering the book title, author or isbn.

Introduction to the First Edition

New polymerisation mechanisms like controlled radical polymerisation are combined with the emulsion polymerisation technique, encountering specific problems but also leading to interesting new possibilities in achieving special nanoscale morphologies with special properties. In the past years many people have been trained in the use of the emulsion polymerisation technique. Many courses on the BSc, MSc and the PhD level as well as special trainings for people in industry are given all over the world. Despite this no recent book exists with the purpose of supporting courses in emulsion polymerisation.

This book is aiming at MSc students, PhD students and reasonably experienced chemists in university, government or industrial laboratories, but not necessarily experts in emulsion polymerisation or the properties and applications of emulsion polymers. For this audience, which is often struggling with the theory of emulsion polymerisation kinetics, this book will explain how theory came about from well-designed experiments, making equations plausible and intuitive. Another issue experienced, especially in industry, is that coupling theory and everyday practice in latex production is really hard. This is another aim of the book; showing how theory works out in real life.

The basis for the contents of this book can be found in the course emulsion polymerisation taught for many years at the Eindhoven University of Technology in the framework of the Foundation Emulsion Polymerisation. Many people have contributed to shaping the aforementioned course and therefore laying a basis for this book: Ian Maxwell, Jenci Kurja, Janet Eleveld, Joop Ammerdorffer, Annemieke Aerdts, Bert Klumperman, Jos van der Loos and last but not least Ton German. Most of the contributors to the chapters are member of the International Polymer Colloids Group, a group of experts around the world that meet on a regular basis and form a unique platform for sharing knowledge in the field.

The book is focussing on emulsion polymerisation in combination with both conventional and controlled radical polymerisation. Except for miniemulsion polymerisation, more exotic techniques like inverse emulsion polymerisation, microemulsion polymerisation and dispersion polymerisation are not covered.

The first chapter is giving a historic overview of the understanding of emulsion polymerisation, also focussing on the solution of the kinetic equations. In the second chapter an introduction is given in the radical (co)polymerisation mechanism, explaining kinetics and the development of molecular weight and chemical composition. In chapter three the basic element of emulsion polymerisation are explained, again focussing on rate of reaction and molecular mass distributions. In chapter four, emulsion copolymerisation, process strategies are explained. In chapter five the implementation of controlled radical polymerisation mechanisms in emulsion polymerisation is discussed. In Chapter 6 the development of morphology in latex production is discussed. Colloidal aspects of emulsion polymerisation are discussed in chapter seven. In chapter eight an overview of the molecular characterization techniques of (emulsion) polymers is given whereas in chapter nine the characterization techniques available for particle size, shape and morphology are reviewed. In Chapter ten and eleven bulk and specialty applications are discussed. As much as possible the nomenclature for polymer dispersions according to IUPAC has been followed (Slomkowski, 2011).

We hope that this book will become a standard textbook in courses in emulsion polymerisation.

Contents