

Monodisperse Emulsions as Template for Highly Structured Polymer Foams

Von der Fakultät Chemie der Universität Stuttgart
zur Erlangung der Würde eines Doktors der
Naturwissenschaften (Dr. rer. nat.) genehmigte Abhandlung

Vorgelegt von

Aggeliki Quell
aus Mannheim

Hauptberichter: Prof. Dr. Cosima Stubenrauch
Mitberichter: Prof. Dr. Michael R. Buchmeiser
Prüfungsvorsitz: Prof. Dr. Frank Gießelmann

Tag der mündlichen Prüfung: 02.12.2016

Institut für Physikalische Chemie
der Universität Stuttgart
2016

Berichte aus der Chemie

Aggeliki Quell

**Monodisperse Emulsions as Template for
Highly Structured Polymer Foams**

D 93 (Diss. Universität Stuttgart)

Shaker Verlag
Aachen 2017

Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at <http://dnb.d-nb.de>.

Zugl.: Stuttgart, Univ., Diss., 2016

Copyright Shaker Verlag 2017

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior permission of the publishers.

Printed in Germany.

ISBN 978-3-8440-4999-2

ISSN 0945-070X

Shaker Verlag GmbH • P.O. BOX 101818 • D-52018 Aachen

Phone: 0049/2407/9596-0 • Telefax: 0049/2407/9596-9

Internet: www.shaker.de • e-mail: info@shaker.de

für *Archonta & Lazaros Mogianni*

Acknowledgments

I would like to express my first and deepest gratitude towards my supervisor *Prof. Dr. Cosima Stubenrauch*. I will always be grateful for the opportunity to do my thesis under her extraordinary supervision. It has been a pleasure to work for and with her. I am also very grateful for all the national and international conferences she enabled me to attend. And most importantly, I will never forget her moral and financial support when I was a visiting scientist at the Ian Wark Research Institute in Adelaide, Australia.

Further, I would like to thank *Prof. Dr. Michael R. Buchmeiser* for being my mentor and second referee for my thesis. I would also like to thank *Prof. Dr. Frank Gießelmann* for accepting the chairmanship during my defense.

I would like to express my gratitude towards *Dr. Wiebke Drenckhan*, *Dr. Sascha Heitkam* and *PD Dr. Thomas Sottmann* for many fruitful discussions during the last three years. Especially Wiebke has supported me and my work in countless ways and I am very thankful for that. Furthermore, I would like to thank *PD Dr. Michael Schweikert* and *Dr. Natalie Preisig* for their support on the TEM measurements as well as *Dr. Alexander Fels* for his support on the SEM measurements. A big thank you goes to the chemical technical assistants *Diana Zauser* and *Birgit Feucht* for their endless support regarding the laboratories.

I am also grateful for the warm welcome and scientific support “The Wark” has given me. Especially *Prof. Dr. Thomas Nann*, *Simon Doe* and *Dipankar Chugh*. Further, I would like to thank my “office mates” for a great atmosphere during my whole stay.

I was very lucky with my students *Jeffrey Appiah* and *Benedetta de Bergolis*. It was a pleasure to supervise them and I wish both of them all the best for their future.

A special thanks goes to my colleagues who have made working here a real treat. Especially my “foamy homies” *Jonas Elsing* and *Sébastien Andrieux* for encouragement and fruitful discussions.

Last but not least, I would like to thank my husband *Sascha Quell* for his support and understanding. And also for funding!

Table of contents

1	Introduction	1
1.1	Motivation	1
1.2	Task description	5
2	Theoretical background	7
2.1	Emulsions	7
2.2	Porous polymers	15
2.3	Microfluidics	25
2.4	Emulsion templating	33
3	Design and calibration of microfluidic chips	39
3.1	Commercially available glass chips	40
3.1.1	Calibration of microfluidic chips	40
3.1.2	Generation of monodisperse emulsions	47
3.2	Self-made glass chips	49
3.2.1	Calibration of microfluidic chips	49
3.2.2	Generation of monodisperse emulsions	53
4	Monodisperse, macroporous polymer foams	55
4.1	Synthesis and characterization	55
4.2	Control of pore morphology	62
4.2.1	Influence of the surfactant concentration	63
4.2.2	Influence of the initiation temperature	67
4.2.3	Influence of the dispersed phase volume fraction	69
4.2.4	Influence of the locus of initiation	72
4.3	Proposed mechanism for formation of different pore morphologies	82
4.3.1	The hypothesis	82
4.3.2	Experimental evidences	85
4.4	Finestructure	93
4.5	Towards graded polymer foams	106
4.6	The limits of single-constriction microfluidics	108

5 Conclusion and outlook	113
6 Experimental section	121
6.1 Devices and materials	121
6.2 Self-made glass chips	123
6.3 Generation and polymerization of the emulsion templates	126
6.4 Characterization of the polymer foams	130
6.4.1 Morphological properties	131
6.4.2 Mechanical properties	131
7 Appendix	135
7.1 Self-made resin chips	135
7.2 Rheological behavior of polydisperse emulsions	140
7.3 Polydisperse polymer foams	147
References	151

Abbreviations and symbols

Abbreviations

AIBN azobis(isobutyronitrile)

DMA dynamic mechanical analysis

DSC differential scanning calorimetry

DVB divinylbenzene

EDGE edge-based droplet generation

EPS expanded polystyrene

FGFM functionally graded foam material

GPC gel permeation chromatography

HIPE high internal phase emulsion

KPS potassium persulfate

LIPE low internal phase emulsion

MCE microchannel emulsification

MIPE medium internal phase emulsion

o/w oil in water

PDMS polydimethylsiloxane

PIBSA poly(isobutylene)succinic anhydride

PIT phase inversion temperature

PS	polystyrene
PU	polyurethane
PVC	polyvinyl chloride
SEM	scanning electron microscopy
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
vol%	volume percent
w/o	water in oil
wt%	weight percent
XPS	extruded polystyrene

Greek symbols

ΔP	Laplace pressure
$\dot{\gamma}$	shear rate
Π	osmotic pressure
Π_{disj}	disjoining pressure
ϵ	strain
η	viscosity
γ	interfacial tension
γ_i	interfacial energy
κ	mean curvature

ρ	density
ρ_{bulk}	bulk density
ρ_{foam}	foam density
σ	stress
φ_{disp}	volume fraction of dispersed phase
ξ	amplitude
$\tan \delta$	damping factor

Numerical

$\bar{2}$	w/o microemulsion co-existing with a water excess phase
$\underline{2}$	o/w microemulsion co-existing with an oil excess phase
1	one-phase microemulsion
3	three-phase microemulsion co-existing with an oil and a water excess phase

Roman symbols

A	area
c	concentration
c_{PS}	polystyrene concentration
c_{surf}	surfactant concentration
Ca	capillary number
d_{drop}	diameter of the water droplet
d_{pore}	diameter of the polymer pore

Abbreviations and symbols

d_{sd} standard deviation of diameters

d_{window} window diameter

E Young's modulus

E_i energy

F force

f frequency

F_A buoyancy force

F_G gravitational force

F_N normal force

G Gibbs free energy

g gravitational acceleration

G' storage modulus

G'' loss modulus

k chemical rate constant

L length

L_α lamellar phase

M molecular weight

m mass

M_n number average molar mass

n amount of substance

p_{cont}	pressure of the continuous phase
P_c	capillary pressure
p_{disp}	pressure of the dispersed phase
PDI	polydispersity index
Q_c	flow rate of continuous phase
Q_d	flow rate of dispersed phase
r	radius
$r_{1,2}$	relative reactivity ratio
r_i	ratio of pore openings
R_f	relative foam density
Re	Raynolds number
T	temperature
t	time
T_g	glass transition temperature
V	volume
v	velocity
W	work
We	Weber number

Abstract

The aim of this work was to synthesize and characterize highly structured monodisperse polymer foams. The task was tackled by combining the traditional concept of emulsion templating with droplet-based microfluidics in order to first generate monodisperse water-in-monomer emulsions and to subsequently synthesize highly structured polymer foams by polymerizing the monomers. This novel technique allowed us for the first time to study systematically the structure-property relationship of the resulting polymer foams. The morphology of the polymer foams was investigated using scanning electron microscopy. The mechanical properties were investigated by measuring the relative foam density and the Young's modulus.

Gathering all results, we conclude that we were able to control the pore morphology and to tune the polymer foam properties by changing the emulsion composition. We had changed independently the initial droplet size, the surfactant concentration, the dispersed phase volume fraction, the initiation temperature as well as the locus of initiation and evaluated the impact of each of these parameters on the resulting polymer foams. Using microfluidics, we also succeeded in producing polymer foams with a defined pore size gradient. By changing the locus of initiation we showed that we can switch between open-cell and closed-cell foams. Open-cell foams were obtained by initiating the polymerization from the bulk phase. Closed-cell foams were obtained by polymerizing from the oil/water interface. Interestingly, the closed-cell foams had a honeycomb-like pore shape whereas the pores of the open-cell foams were spherical. This remarkable effect on the pore morphology was investigated further and after extensive experimental proof we proposed a new mechanism, explaining the link between locus of initiation and pore morphology. It was found that a strong osmotic transport redistributes matter from the denser pockets of sphere packing into the struts of the polymer foam. This osmotic transport only occurs in interface initiated systems and does not occur in bulk-phase initiated systems. The results obtained from varying the template parameters and the knowledge about the mechanism are expected to give new insights about the tuning possibilities of emulsion templating and may open a new arena for tailor-made polymer foams.

Kurzzusammenfassung

Ziel dieser Arbeit war die Synthese und Charakterisierung hochgeordneter monodisperser Polymerschäume. Um diese Aufgabe zu erfüllen, wurde das traditionelle Konzept emulsionsbasierter Template mit der Mikrofluidik verheiratet. Diese Kombination ermöglichte uns zum ersten Mal die Herstellung monodisperser Wasser-in-Monomer Emulsionen, deren Polymerisation zu hochgeordneten monodispersen Polymerschäumen führte. So gelang es erstmals die Struktur-Eigenschafts-Beziehung der Polymerschäume gezielt zu untersuchen. Die Morphologie der Polymerschäume wurde mittels Rasterelektronenmikroskopie untersucht. Die mechanischen Eigenschaften hingegen wurden über die Bestimmung der relativen Schaumdichte und des Elastizitätsmoduls bestimmt.

Werden alle Ergebnisse zusammengefasst, zeigte sich, dass sowohl die Morphologie als auch die mechanischen Eigenschaften der Polymerschäume über das Variieren der Emulsionsparameter gezielt eingestellt werden konnten. Es wurden die Tropfengröße der Emulsion, die Tensidkonzentration, der Volumenanteil an dispergierter Phase, die Initiierungstemperatur sowie der Ort der Initiation verändert und der Einfluss dieser Parameter auf die Polymerschäume untersucht. Ferner konnte durch den Einsatz der Mikrofluidik erstmals ein definierter Porengradient im Polymerschäum eingestellt werden. Durch Ändern des Ortes der Initiation von der kontinuierlichen Phase zur Öl/Wasser Grenzfläche wurde gezeigt, dass sowohl offenzellige und geschlossenzellige Polymerschäumen hergestellt werden können. Grenzflächeninitiation führte zu geschlossenzelligen Schäumen während die Initiation aus der kontinuierlichen Phase zu offenzelligen Schäumen führte. Interessanterweise zeigten die Poren geschlossenzelliger Schäume eine honigwabenähnliche Struktur und die Poren offenzelliger Schäume waren sphärisch. Dieser bemerkenswerte Unterschied wurde untersucht und nach vielen experimentellen Beweisen wurde ein neuer Mechanismus vorgeschlagen, welcher den Zusammenhang zwischen der Morphologie des Polymerschäums und dem Ort der Initiation erklärt: Ein osmotisches Transportphänomen transportiert Material aus den Zwischenräumen der Kugelpackung in die Kontaktstellen zwischen die Poren. Dieser Materialtransport findet nur bei Grenzflächeninitiation statt. Die Ergebnisse aus der Templatevariation sowie die Kenntnis über den Entstehungsmechanismus der Morphologie gibt neue Anreize zur Variationsmöglichkeit der Emulsionstemplate und ebnet den Weg für die Herstellung anwendungsspezifischer Polymerschäume.