

Conference Guide



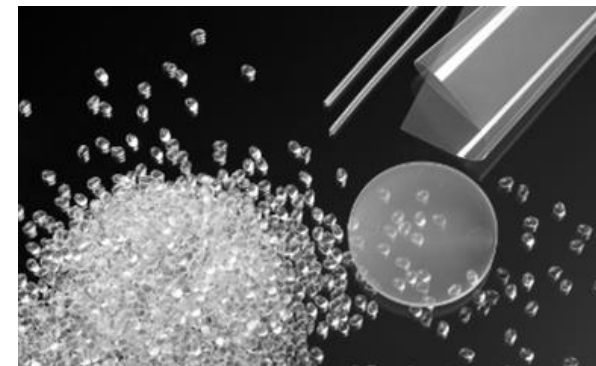
TECHNISCHE
UNIVERSITÄT
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UNIVERSITY OF
CHEMISTRY AND
TECHNOLOGY
PRAGUE

7th PhD-Workshop on Polymer Reaction Engineering

31st August to 2nd September 2018 in Prague



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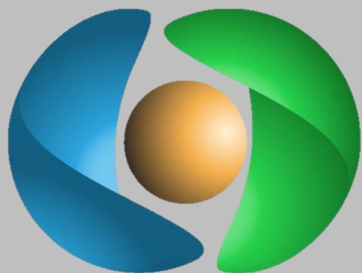
 **Novolen**
TECHNOLOGY

 **MCDERMOTT**
TECHNOLOGY

سابك
sabik

synthomer 

WILEY



Welcome to the 7th PhD-Student Workshop on Polymer Reaction Engineering

Dear PhD-students, professors and company representatives,

the PhD-Student Workshop on Polymer Reaction Engineering represents an international platform where young researchers in the field of polymer reaction engineering have the opportunity to get into contact with fellow PhD-students but also to meet various industry representatives and potential employers personally. Moreover, PhD-students can benefit from useful feedback on their work and improve their soft skills by practicing the presentation of complex scientific topics.

The workshop is being held for the seventh time now. It has been launched in Lyon in 2012 with a total number of 35 participants. The second workshop has been organized in Hamburg. The third one took place in San Sebastian and in 2015 we met in Fürstenfeldbruck near Munich. The WPPRE student workshop in 2016 was hosted again by the University of Hamburg. Last year we recorded a number of 41 registrations in Vienna. In this year we are expecting 45 participants from universities as well as industry.

Having participants from ten universities and various research fields we can look forward to an interesting and diverse workshop whose contributions include the following topics:

- new process set-ups as well as new methods of inline-spectroscopy
- synthesis of homopolymers, copolymers, blends and hybridpolymers
- bulk-, emulsion-, catalytic- and high-pressure polymerization

- modeling of chemical reaction networks: Monte Carlo- and CFD-simulations as well as the consideration of compartmentalization
- focusing on structure-property relationships and thermodynamics

With all these topics ahead we are looking forward to an informative workshop in Prague with you.

The Organizing Committee

Organizing Committee

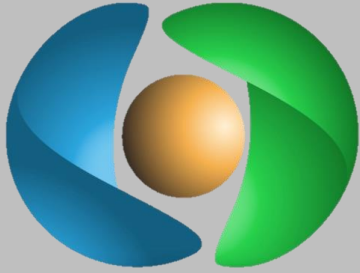
Markus Busch	Chair of WPPRE, TU Darmstadt
Juraj Kosek	University of Prague
Werner Pauer	Secretary of WPPRE, Universität Hamburg
Paul Peikert	TU Darmstadt
Kristina Pflug	TU Darmstadt
Lenka Krajáková	University of Prague

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General Information

Language

The official language at the workshop is English.

Insurance

The organizers do not accept responsibility for individual medical or personal insurance. Participants are strongly advised to take out their own insurance policies.

Telephone

The international code for Czech Republic is +42.

Emergency phone numbers

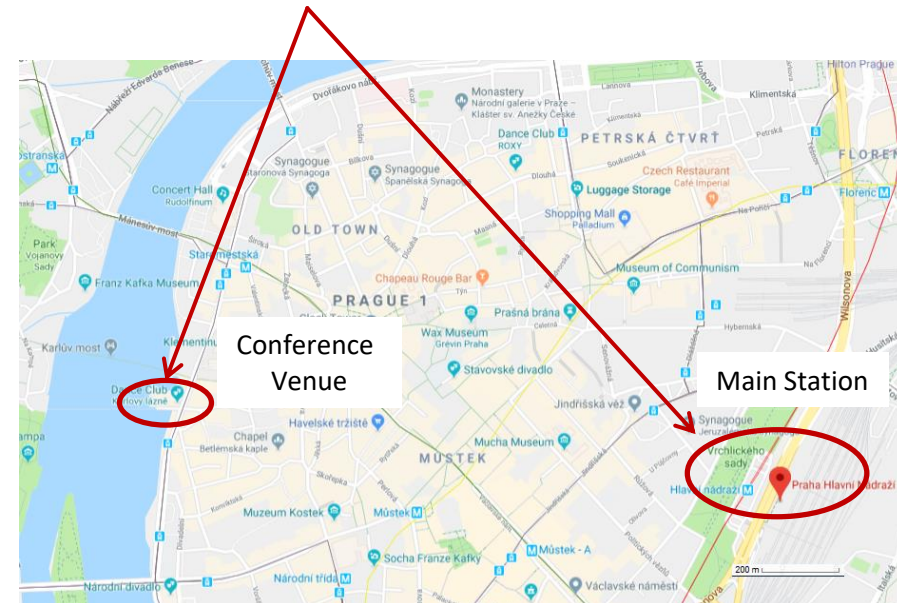
General Emergency Number	112
Firebrigade	150
Police	158
Prague City Police	156
Ambulance	155

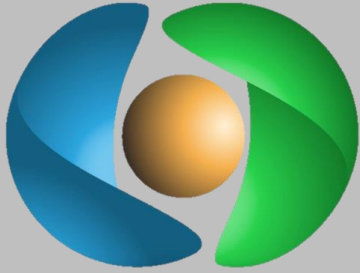
Taxi numbers

(+42) 0 732 52 47 42
(+42) 222 333 222
(+42) 257 257 257

Main Station

Wilsonova 300/8, 120 00 Vinohrady-Praha 2 (main station)





Arrival in Prague: Public Transport & Your Way to the Workshop

Transfer from the Airport to the Venue

There are three possibilities to get to Prague's old quarter. Taking public busses to the main station of Prague takes approximately 30 minutes. Hereby, bus numbers 100 and 119 are recommended. However, public busses do not drive at night from the airport. Furthermore, it is also possible to the Airport Express. Of course also a taxi can be taken (approx. 25 minutes).

From the inner city the Conference Venue can easily be reached by foot.

Workshop Venue Address

Novotného lávka
110 00 Praha 1-Staré Město

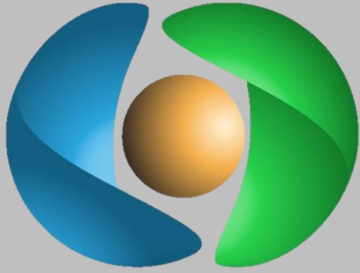
Contact

If you have any further questions, please feel free to contact us via email or visit our homepage.

wppre@pre.tu-darmstadt.de

http://efce.info/PhDStudent_Workshop_WPPRE.html





Places to know

Places to Know – Addresses and Meeting Points

Conference Venue

Novotného lávka 110 00 Praha 1-Staré Město

Medieval Dinner: Dinner on Friday

Central Prague Křižovnické náměstí 191/3, Prague 1

Lunch at Restaurant Lavka on Saturday

Novotneho Lavka 201/1, Prague 110 00

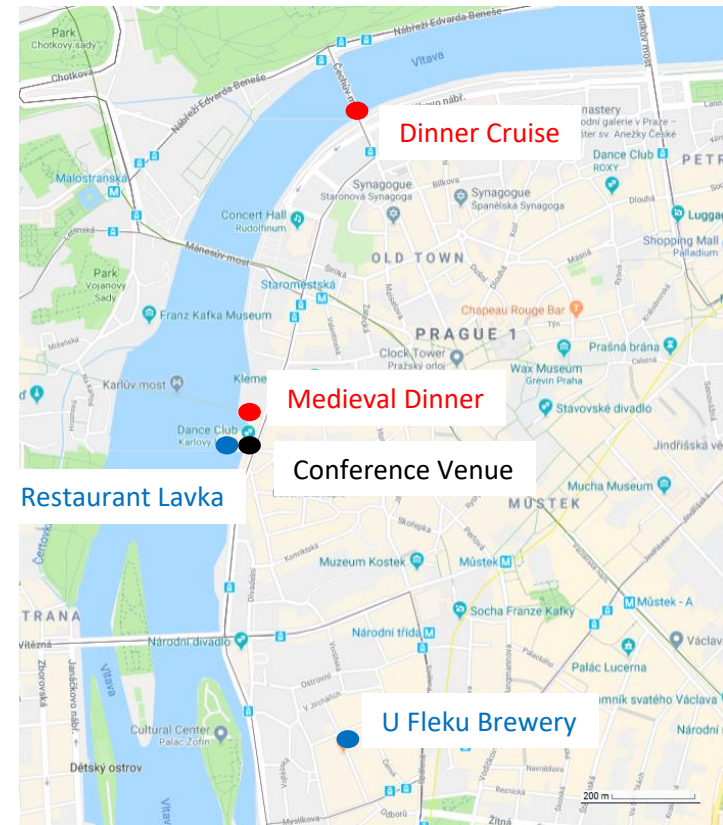
Dinner Cruise on Vltava River on Saturday

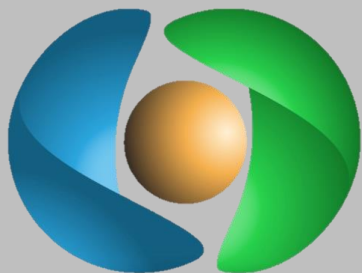
Meeting Point: Čechův Bridge

Lunch at U Fleku Brewery on Sunday

Křemencova 11, 110 00 Nové Město

Prague Inner City, Overview





Program by Days

Friday, 31st August 2018

14:00 -15:00 **Registration at the conference site**
Poster wall preparation

15:00 -15:15 **Welcome**
Prof. Dr. M. Busch, Prof. Dr. J. Kosek

~~~~~*Session I: New Materials*~~~~~

Chair: Verena Schamboeck (University of Amsterdam)

15:15 -15:35 **Jack van Schijndel** (Eindhoven University of Technology)
Lignin-Derived Chemically Recyclable Aromatic Polyesters

15:35 -15:55 **Fabian Wenzel** (University of Basque Country)
to be announced

15:55 -16:15 **Mareike Bendig** (University of Hamburg)
Effects of the Emulsion Polymerization Process on the Efficiency of Barrier Coatings

16:15 -16:35 **Noushin Rajabalinia** (University of Basque Country)
Quantitative Morphology Characterization of Synthesized Structured Polymer Particles via Seeded Emulsion Polymerization

16:35 -17:30 **Coffee Break and Poster Session**



17:30 -18:00 **Borealis**

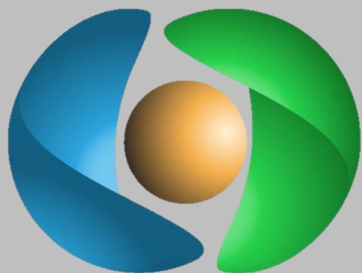
19:30 **Medieval Dinner**
Meeting Point at Charles Bridge

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Program by Days

Saturday, 1st September 2018

Session II: Modelling

Chair: **Jorik Hill** (Martin-Luther-University Halle-Wittenberg)

- 09:00 – 09:20 **Paul Peikert** (TU Darmstadt)
Modelling of Ethene High-Pressure Homo- and Co-Polymerization
- 09:20 - 09:40 **Verena Schamboeck** (University of Amsterdam)
The Effect of Euclidean Space on Graph-Like Models of Hyperbranched Polymer Networks
- 09:40 – 10:00 **Sebastian Eller** (University of Hamburg)
Simulation of a Stirring Disc Reactor used for Highly Viscous and Multiphase Polymerizations
- 10:00 – 10:20 **Oliver Salman** (TU Darmstadt)
Implementation of Compartmentation in Kinetic LDPE-Models to Describe Mixing Effects in the Reaction Network

Coffee Breaks
and City Ralley
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10:20 - 11:00

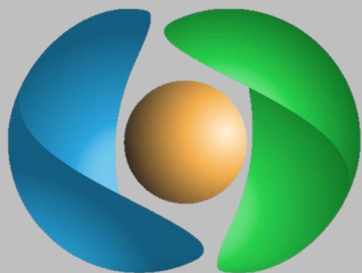
Coffee Break and Poster Session



Session III: Polyolefines

Chair: **Sebastian Eller** (University of Hamburg)

- 11:00 – 11:20 **Gerold Rittenschober** (Johannes Kepler University, Linz)
Synthesis of Polypropylene for 3D-Printing Applications
- 11:20 – 11:40 **Jorik Hill** (Martin-Luther-University Halle-Wittenberg)
Heat Transfer Effects in the Gas Phase Polymerization of Propylene



Program by Days

Saturday, 1st September 2018

11:40 - 12:00 **Julia Eigenseer** (TU Darmstadt)
Continuous Solution Polymerization as a Tool for Metallocene Catalyzed Homo- and Co-Polymerization Investigation

12:00 - 12:20 **Simon Jantač** (University of Prague)
Study of Unipolar and Bipolar Charging of Polyethylene Powders

12:20 -12:50 **Thomas Kroener (Novolen)**
Lummus Novolen Technology: Working for a Polypropylene licensor.

13:00 **Lunch**
Restaurant Lávka
Novotneho Lavka 201/1, Prague 110 00, Czech Republic

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~~~~~ Session IV: Thermodynamics ~~~~~

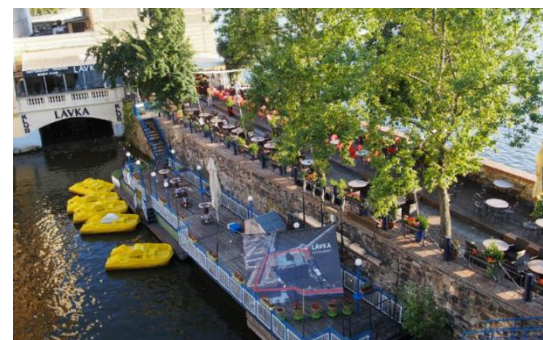
Chair: **Gerold Rittenschober** (Johannes Kepler University, Linz)

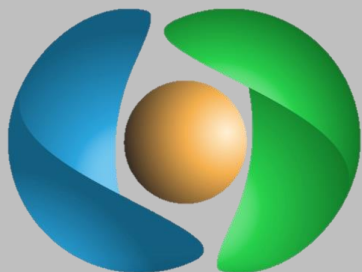
14:30 - 14:50 **Lenka Krajkova** (University of Prague)
Sorption Equilibria Relevant for Catalytic Olefin Polymerization

14:50 – 15:10 **Sabrine Kardous** (University Lyon 1 - LAGEP)
Thermodynamics Effects on the Reaction Rate in Gas Phase Polyolefin Reactions

15:10 - 15:30 **Patrik Schneider** (University of Prague)
Sorption of Liquid in Polyethylene Measured by Low-Field NMR

15:30 – 15:50 **Tobias Meller** (University of Hamburg)
Design and Characterization of a Gas-Solid Reaction Calorimeter





Program by Days

Saturday, 1st September 2018

15:50 – 16:30 **Coffee Break and Poster Session**



17:40 – 18:10 **Danny Antes (Synthomer)**

16:30 – 17:00 **Wolfgang Gerlinger (BASF)**
PRE in R&D and for optimization of polymer(ization)s

19:00 **Dinner Cruise at Vltava River**
Starting Point: Pier 5, Dvořákovo Nábřeží under the Čechův Bridge

Session V: New Processes

Chair: Sabrina Kardous (University Lyon 1 - LAGEP)

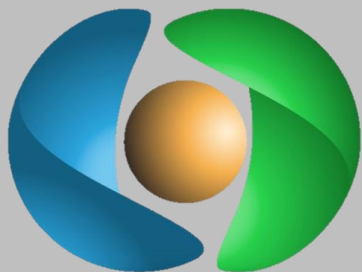
17:00 – 17:20 **Manis Gheghiani (University Lyon 1 - LAGEP)**
Coupling of Multispectral Sensors to Monitor Emulsion Polymerization Processes

17:20 – 17:40 **Mirko Düvell (University of Hamburg)**
Micro Reaction Engineering: Investigation of Pressure Drop and Heat Transfer of the Miprowa[®] Lab Reactor



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Program by Days

Sunday, 2nd September 2018

09:15 **Departure at Conference Venue**

09:45 **City Rally - Prague**
Meeting point:
to be announced



12:30 **Maryam Khodadadian (Sabic)**

12:30 **Poster Prize and Closing Ceremony**

The Prize for the Best Contribution is kindly
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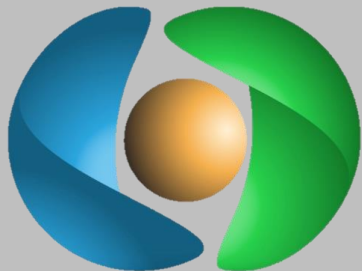
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13:00 **Lunch at U Fleků Brewery and Restaurant**
Křemencova 11, 110 00 Prague 1



Lunch kindly sponsored by

سابك
sabic



List of Posters

1. Modeling of Ethyl Linoleate Polymerization for Better Understanding of the Drying Process of Oil Paint

Yuliia Orlova, I. Kryven and P. Iedema

2. Implementation of Compartmentation in Kinetic LDPE-Models to Describe Mixing Effects in the Reaction Network

Oliver Salman, A.Rott, M. Busch

3. Modelling of High-Pressure Ethene Homo- and Co-Polymerization

Paul Peikert, K. Pflug, M. Busch

4. The Effect of Euclidean Space on Graph-Like Models of Hyperbranched Polymer Networks

Verena Schamboeck, I. Kryven, P. D. Iedema

5. Simulation of a Stirring Disc Reactor used for Highly Viscous and Multiphase Polymerizations

Sebastian Eller, G.A. Luinstra

6. Evaluation and Synthesis of Chemical Blowing Agents for the Development of Light Weight Acrylate-Based 3D Printing Inks

Lukas Göpperl, A. Kreuzer, C. Paulik

7. Study of Unipolar and Bipolar Charging of Polyethylene Powders

Simon Jantač, L. Konopka, M. Vrzáček, L. Kolářová, J. Kosek⁵

8. Micro reaction engineering: Investigation of Pressure Drop and Heat Transfer of the Miprowa[®] Lab Reactor

Mirko Düvell, W. Pauer, H.-U. Moritz

9. Heat Transfer Effects in the Gas Phase Polymerization of Propylene

Jorik Hill, M. Bartke

10. A New Approach to Stopped-Flow Reactions for Slurry and Gas-Phase Olefin Polymerization

Yashmin Rafante Blazzio, T. McKenna

11. Polymerization Kinetics of Ziegler-Natta PP Catalysts

Daniel Pernusch, C.Paulik

12. Effect of Hydrogen Partitioning on Homo-Propylene Polymerization Kinetics

Sina Valaej, A. Drawateep, M. Bartke

13. Sorption of Liquid in Polyethylene Measured by Low-Field NMR

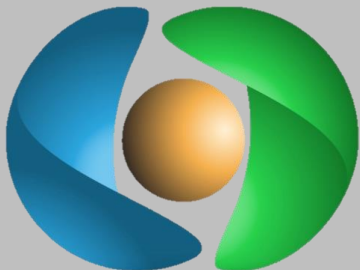
Patrik Schneider, T. Chaloupka, J. Kosek

14. Sorption Equilibria Relevant for Catalytic Olefin Polymerization

Lenka Krajáková, M. Podivinská, J. Kosek

15. Impact of Condensing Agents in Different Temperatures in the Gas Phase Polymerisation of Ethylene

Fabiana N. Andrade, T. F.L. McKenna



List of Posters

16. Experimental and Modeling Study of Ethylene Polymerization in Gas Phase Reactors

Amel Ben Mrad, T. F. L. McKenna

17. Kinetics and Product Properties of the Ethylene Polymerization with Five Different Bisimine Pyridine Iron Catalysts

Elsa Schoeneberger, G. A. Luinstra

18. Continuous Solution Polymerization as a Tool for Metallocene Catalyzed Homo- and Co-Polymerization Investigation

Julia Eigenseer, M. Busch

19. Modelling of a Solution Polymerization Mini-Plant

Maria Dernbach, J. Eigenseer, M. Busch

20. A New and Simple Method to Obtain Easily and Quickly Kinetic and Thermodynamic Data via *Online* FTIR-Spectroscopy

Sarah-Franziska Stahl, J. Marbach, G. A. Luinstra

21. In-line Monitoring of Growth of Nano-Scaled Particles and Droplets in Concentrated Liquid Dispersions by Photon Density Wave Spectroscopy

Stephanie Schlappa, M. Muenzberg, O. Reich, R. Hass

22. In-Line Monitoring of Phase Inversion Temperature Polymerization of Styrene with Photon Density Wave Spectroscopy and Particle

Scott Kilbride, M. Münzberg, O. Reich, R. Hass

23. Quantitative Morphology Characterization of Synthesized Structured Polymer Particles via Seeded Emulsion Polymerization

Noushin Rajabalinia, S. Hamzehlou, E. Modin, A. Chuvilin, J. R. Leiza, J. M. Asua

24. Effects of the Emulsion Polymerization Process on the Efficiency of Barrier Coatings

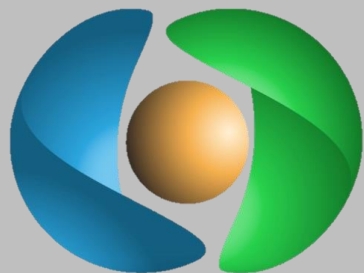
Mareike Bendig, H.-U. Moritz, W. Pauer

25. To be announced

Fabian Wenzel, M. Aguirre, L. Pardo, J. R. Leiza

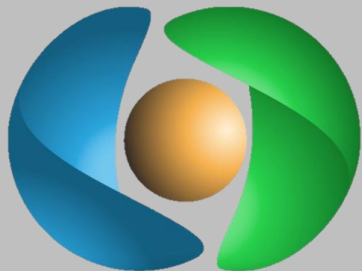
26. Design and Characterization of a Gas-Solid Reaction Calorimeter

Tobias Meller, H.-U. Moritz, W. Pauer



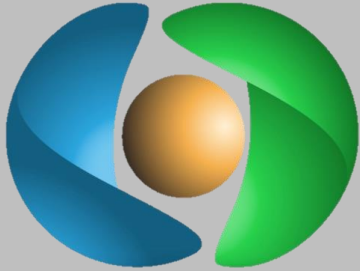
List of Participants

	First Name	Surname	Institution
1.	Nouredine	Ajellal	Borealis
2.	Mohammad	Al-haj Ali	Borealis
3.	Danny	Antes	Synthomer
4.	Amel	Ben Mrad	C2P2 (CPE Lyon)
5.	Mareike	Bendig	University of Hamburg
6.	Yashmin	Blazzio	Université Claude Bernard Lyon 1
7.	Markus	Busch	TU Darmstadt
8.	Maria	Dernbach	TU Darmstadt
9.	Mirko	Düvell	University of Hamburg
10.	Julia	Eigenseer	TU Darmstadt
11.	Sebastian	Eller	University of Hamburg
12.	Wolfgang	Gerlinger	BASF
13.	Manis	Ghedhiani	University Lyon 1 - LAGEP



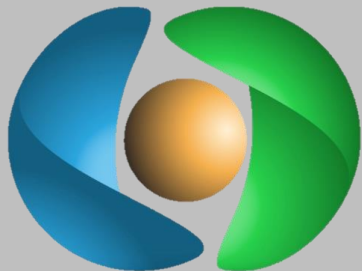
List of Participants

	First Name	Surname	Institution
14.	Lukas	Göpperl	Johannes Kepler University
15.	Eric	Grolman	DSM
16.	Jorik	Hill	Martin-Luther-University Halle-Wittenberg
17.	Jaakko	Hyvönen	Borealis
18.	Simon	Jantač	University of Chemistry and Technology, Prague
19.	Sabrine	Kardous	University Lyon 1 - LAGEP
20.	Maryam	Khodadadian	Sabir
21.	Scott	Kilbride	Universität Potsdam
22.	Juraj	Kosek	University of Chemistry and Technology Prague
23.	Lenka	Krajkova	University of Chemistry and Technology Prague
24.	Thomas	Kroener	Novolen
25.	Julian	Laackmann	Evonik
26.	Tobias	Meller	University of Hamburg



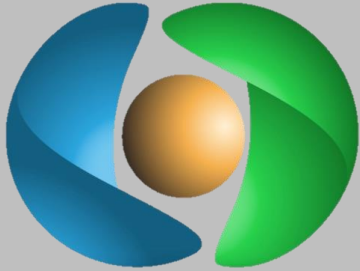
List of Participants

	First Name	Surname	Institution
27.	Fabiana	N Andrade	University Lyon 1
28.	Yuliia	Orlova	University of Amsterdam
29.	Nida	Othman	University of Lyon
30.	Werner	Pauer	University of Hamburg
31.	Christian	Paulik	Johannes Kepler University
32.	Paul	Peikert	TU Darmstadt
33.	Daniel	Pernusch	Johannes Kepler University
34.	Kristina	Pflug	TU Darmstadt
35.	Noushin	Rajabalinia	University of the Basque country
36.	Gerold	Rittenschober	Johannes Kepler University
37.	Oliver	Salman	TU Darmstadt
38.	Verena	Schamboeck	University of Amsterdam
39.	Stephanie	Schlappa	University of Potsdam / InnoFSPEC



List of Participants

	First Name	Surname	Institution
40.	Patrik	Schneider	University of Chemistry and Technology, Prague
41.	Elsa	Schoeneberger	University of Hamburg
42.	Stefan	Spiegel	Wiley-VCH
43.	Sarah-Franziska	Stahl	University of Hamburg
44.	Sina	Valaei	Martin Luther University
45.	Jack	van Schijndel	Eindhoven University of Technology
46.	Fabian	Wenzel	POLYMAT, University of the Basque Country UPV/EHU



Book of Abstracts

1. Jack van Schijndel
2. Mareike Bendig
3. Noushin Rajabalinia
4. Paul Peikert
5. Verena Schamboeck
6. Sebastian Eller
7. Oliver Salman
8. Gerold Rittenschober
9. Jorik Hill
10. Julia Eigenseer
11. Simon Jantač
12. Lenka Krajakova
13. Sabrine Kardous
14. Patrik Schneider
15. Tobias Meller
16. Mani Gheghiani
17. Mirko Düvell
18. Yuliia Orlova
19. Lukas Göpperl
20. Yashmin Blazzio
21. Daniel Pernusch
22. Sina Valaei
23. Fabiana N Andrade
24. Amel Ben Mrad
25. Elsa Schoeneberger
26. Maria Dernbach
27. Sarah-Franziska Stahl
28. Stephanie Schlappa
29. Scott Kilbride

Lignin-derived chemically recyclable aromatic polyesters

Jack van Schijndel^{ab}, Jan Meuldijk^b*

^a *Research Group Biopolymers/Green Chemistry, Centre of Expertise BioBased Economy, Avans University of Applied Science, Lovensdijkstraat 61, 4818 AJ Breda, The Netherlands*

^b *Department of Chemical Engineering and Chemistry, Lab of Chemical Reactor Engineering/Polymer Reaction Engineering, Eindhoven University of Technology, Den Dolech 2, 5600 MB Eindhoven, The Netherlands*

Lignin is the major component in wood and the second most abundant naturally occurring polymer. The extraction of lignin from wood is common practice in the paper pulping industry. While lignin is currently used as a filler or additive, it is rarely exploited as a raw material for chemical production. However, its highly functional character (i.e. rich in phenolic and aliphatic hydroxyl groups) constitutes an attractive renewable feedstock for aromatic components.

Polyethylene terephthalate (PET) is the third most common synthetic polymer. The design of biobased PET mimics, which exhibit similar thermal and gas permeability properties, will probably require aromatic components. Since we produce plastics by chemical processes, it may be obvious that the way they are treated at the end of their technical lifetime is also chemical. Chemical recycling recovers the monomers from the polymeric material. In this way, the valuable chemical information is not lost in contrary when it's converted to CO₂ and H₂O by incineration or microbial conversion. This has motivated us to search for mild conversion processes of polymers into their building blocks, i.e. the monomers. Biobased PET analogs were therefore synthesized from lignin-derived renewable starting materials via transesterification reactions. During the synthesis and de-polymerisation, there was a special focus on applying non-toxic reagents in order to meet the requirements of green chemistry.

Your notes:

Effects of the emulsion polymerization process on the efficiency of barrier coatings

M. Bendig, H.-U. Moritz, W. Pauer

*University of Hamburg / Institute of Technical and Macromolecular Chemistry, Bundesstraße 45,
20146 Hamburg, Germany*

Polymer dispersions are widely used as coatings for paper and paperboard. In order to improve the understanding of barrier coatings it is important to know which factors affect the barrier properties qualitatively and quantitatively. Moreover, aqueous polymer dispersions have to be free of volatile organic compounds (VOC). Furthermore, products with food contact are restricted by the Food and Drug Administration (FDA, USA) and are subject to regulations. Thus, not every monomer or additive can be used.

Commonly used monomers in emulsion polymerization are styrene, butadiene, vinyl acetate as well as various acrylates.¹ The main focus in the subject of coated paper are the glossiness, the smoothness or the ink absorbability.² Since the recycling of waste is getting more and more important, the usage of paper as a packaging material is going to be more significant. A coating on food packaging needs to be water resistant and resistant to grease. These two conflicting properties should be combined in one coating. To expand the field of application for polymer dispersions as barrier coatings, the influence of different parameters of the polymerization process were analyzed, e.g. the emulsifier, the addition of a third monomer and the viscosity of the dispersion. As it is hard to attribute the performance of commercial products to a certain component, polymer dispersions were synthesized by emulsion polymerization. The emulsifier concentration and type were varied as well as the monomer type and the monomer ratio.

Emulsion polymerization was used to produce mainly styrene-butyl acrylate copolymers. While butyl acrylate provides hydrophobicity, styrene should enhance thermal stability. In this system the glass transition temperature can be adjusted in a wide range. Copolymers with a high (> 50 °C) glass transition temperature form brittle films, while copolymers with a low (< 0 °C) glass transition temperature form sticky films. The minimum film formation temperature (MFFT) is highly dependent on the glass transition temperature. It was determined with a minimum film formation temperature bar. As well as the glass transition temperature, the MFFT only shows a dependence on the monomer ratio. Since the emulsifier plays a key role in the effectiveness of water resistance, the reduction of the emulsifier concentration in the emulsion polymerization was analyzed. In terms of water resistance, a dispersion with almost no emulsifier might be the best opportunity. In this case the stability of the dispersion is insufficient.

In order to find a balance between a stable dispersion and an efficient barrier against water, the emulsifier concentration could be decreased to five times the critical micelle concentration even with a higher monomer content. The monomer concentration was increased stepwise from 20 to 40 weight percent. Contact angle measurements show that a reduced emulsifier concentration lead to higher contact angles around 100 ° and more stable contact angles with regard to a time period of 60 s compared to the paper itself. This indicated an increased water resistance of the coating. As the paper itself has been hydrophobic, the coating of a hydrophobic binder was consistent. The influence of glycidyl methacrylate as a third comonomer on the film formation and the stability of the dispersion was analyzed to find a way to create barrier coatings with a water and grease resistance at the same time.

To further enhance the stability of the dispersion, an ionic surfactant as well as a non-ionic surfactant were used during the polymerization. The polymer latex stabilized by the non-ionic surfactant showed a better stability according to pH fluctuations or addition of fillers. Here a longer reaction time was needed. Overall, these results offer a better understanding how the barrier properties of coatings work. In order to shorten the nucleation period of the polymerization process and to increase the stability of the dispersion at the same time, a combination of ionic and non-ionic surfactant was used. Especially the stability when adding a filler is important to process the dispersion. Hydroxyl ethyl cellulose (HEC) can be added to adjust the viscosity of the dispersion, as the viscosity is one of the main elements when applying a coating to a substrate. With the addition of two weight percent of HEC the viscosity can be increased from around 4 mPas to 400 – 500 mPas.

1. Andersson, C. New ways to enhance the functionality of paperboard by surface treatment—a review. *Packag. Technol. Sci.* (2008). doi:10.1002/pts
2. Duan, H., Zhao, C., Wu, Y. & Zhang, Q. Performance in Paper Coating of Styrene / Acrylate Copolymer Latex. **81**, 78–81 (1999).

Your notes:

Quantitative morphology characterization of synthesized structured polymer particles via seeded emulsion polymerization

Noushin Rajabalinia¹, Shaghayegh Hamzehlou¹, Evgeni Modin², Andrey Chuvilin^{2,3}, Jose R. Leiza¹, José M. Asua¹

¹*POLYMAT, University of the Basque Country UPV/EHU, Avda Tolosa 72, 20018 Donostia-San Sebastián, Spain*

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Structured polymer particles, which combine the positive properties of their components and avoid their drawbacks, have received a great interest in the wide demanding cases of industrial and medical applications including adhesives and coatings, energy storage and gene and drug delivery. The performance and application of the structured particles latex are directly affected by their morphology, however the knowledge-based strategies to develop particles with well-controlled morphologies are not clearly developed. The reason is that the effect of different reaction parameters controlling the final morphology such as glass transition temperature of the phases, reaction temperature, initiator type and others are not quantified yet. On the other hand, accurate characterization of complex morphologies using available techniques is still a challenge.

In the current work, two-phase polymer-polymer structured latex particles of a copolymer of hydrophilic and hydrophobic monomers were synthesized by seeded semibatch emulsion polymerization. The effect of different reaction parameters on the final morphology such as softness or hardness of the seed, type of initiator and crosslinker agent were studied. Different characterization techniques were used to assess kinetics, microstructure and morphology of the produced polymer latexes with the aim of accurate understanding the dynamics of the of particle morphology development. An image analysis technique based on the HAADF STEM tomography was used to give 3D projection of the final morphologies, which yields a precise description of the particle morphology from where the distributions of the phases can be quantitatively obtained. Later the experimental data was used to validate parameters of already developed mathematical model [1] to predict the particle morphology.

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Your notes:

Modelling of High-Pressure Ethene Homo- and Co-Polymerization

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In 2015 the annual global production of synthetic plastics amounted to 322 million tons.^[1] About one third of industrially produced polymers can be assigned to polyethylene (PE) which exhibits a simple polyolefin structure. In dependence on its branching structure polyethylene can be divided into different types. Hereby, Low Density Polyethylene (LDPE) represents the most commonly produced and consumed plastic material.^[1]

LDPE's unique macroscopic properties largely depend on the branching structure as well as on the employed co-monomer. The reason for its outstanding processing properties is that LDPE and its co-polymers exhibit short-chain branches (SCBs) as well as long-chain branches (LCBs). In order to predict those properties, the branching structure is still centre of current research.

Due to its extraordinary process conditions at high pressures up to 3000 bar and temperatures up to 300 °C, performing a sensitivity analysis regarding to the boundary conditions of the polymerization proved to be time and cost intensive. Therefore product development and process optimization is frequently aided by modelling.

Commonly performed simulation of the free radical polymerization is done numerically. As a result of solving differential equations describing the kinetics as well as balances (heat, mass and impulse) a deterministic simulation only calculates mean values for branching densities. However, if the microstructure is of interest, stochastic modelling, so called Monte-Carlo simulations, are necessary. A stochastic calculation of the individual molecular topology is based on choosing random numbers to determine the sequence of reaction steps resulting in a polymeric chain in the end. In our working group *Neuhaus*^[2] developed a coupled deterministic and stochastic simulation approach to model the polymeric microstructure which has been extended by *Eckes*^[3].

The present study is based on that hybrid approach. *Eckes*^[3] validated his model for homo-polymerizations of ethene in autoclaves which has been expanded by a copolymerization approach in this present work. That newly developed coupled deterministic and stochastic simulation approach for considering high-pressure ethene co-polymerizations is not limited to a certain co-monomer. Furthermore, reactor modelling is also not restricted to the reactor type. Therefore the microstructure of diverse LDPE-co-polymers being produced in tubular reactors, autoclaves as well as reactor combinations can be determined.

Within this work the newly developed model has been validated successfully for an industrial tubular reactor as well as for a multi-zone autoclave. Modelling results exhibit an excellent accordance between deterministically and stochastically calculated mean values (e.g. for branching densities and for co-monomer content). On top of that, a new memory efficient way to store each position of a co-monomer in a chain has been introduced. In combination with the storage of the topological structure it is possible to capture configurational information for ensembles up to 40 million molecules.

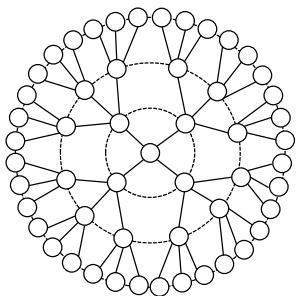
Stored data can then afterwards be used to obtain molecular properties. Besides determining the molecular weight distribution or mean values (e.g. for branching densities) the newly developed hybrid approach can be used to describe the distribution of ethene and a co-monomer in the macromolecules. Furthermore, the stored information can be employed as input for rheological models (e.g. from *Read* and *Leish*^[4]) or to calculate contraction factors as well as the radius of gyration. Hereby, a 3D-random-walker has been improved by considering a bond angle dependence as well as self-avoiding behaviour. Thus, a more realistic calculation of the radius of gyration in dependence on the chain length with regard to differently branched polymers is enabled.

In conclusion, the developed hybrid approach in combination with evaluation routines like the self-avoiding random-walker are excellent examples for tools to perform simulation aided product design in order to receive a product with defined properties.

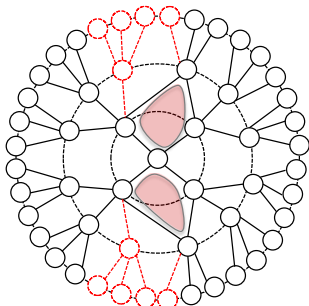
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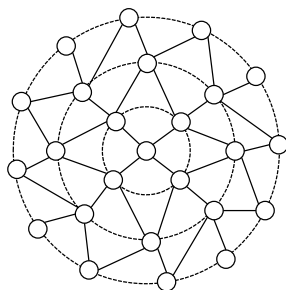
Your notes:



Exponential growth



Cyclization



Algebraic growth

Your notes:

The effect of Euclidean space on graph-like models of hyperbranched polymer networks

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Since the development of the first models for hyperbranched polymer networks by Flory, there is a heated discussion about the effects of three-dimensional space on polymer networks. Flory's model¹ and many models developed afterwards, e.g. random graphs, assume a tree-like structure in the sol and infinite cycles in the gel. For instance, for functionality $f=3$ the percolation threshold is predicted to be $p=0.5$. These assumptions, however, predict (1) no small cycles and (2) exponential growth with the number of generations when explored from an arbitrary node. Another alternative is lattices, which predict a higher percolation threshold than Flory and are space-embeddable, but the percolation threshold strongly depends on the chosen lattice. Additionally, Eichinger proposed a model that predicts no percolation for $f=3$.²

We propose a model that features algebraic growth of the networks and yields a constant density in Euclidean space while still sustaining random structures (in contrast to lattices). By not constraining the number of parents of a node we allow cyclization in the network. The model was developed as an extension of our previous work.³

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Simulation of a stirring disc reactor used for highly viscous and multiphase polymerizations

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Polymerization processes in solvents often struggle with high viscosities resulting from the formation of the long chain products. The mixing of the reactants aggravates, which may lead to hot spots and consequently to low value products. High shear forces need to be applied to ensure a well-mixed reaction medium. A continuously stirred tank reactor (CSTR) is commonly used, but common stirrers can only operate in either highly viscous media, but with a low shear force induction, or vice versa. Additionally, the stirrers have only contact to a small fraction of the reaction medium and satisfactory mixing is therefore limited to a small region within the reaction medium.

A possible alternative to overcome this challenge is a multistage stirring disc reactor (SDR), which is shown in Figure 1.

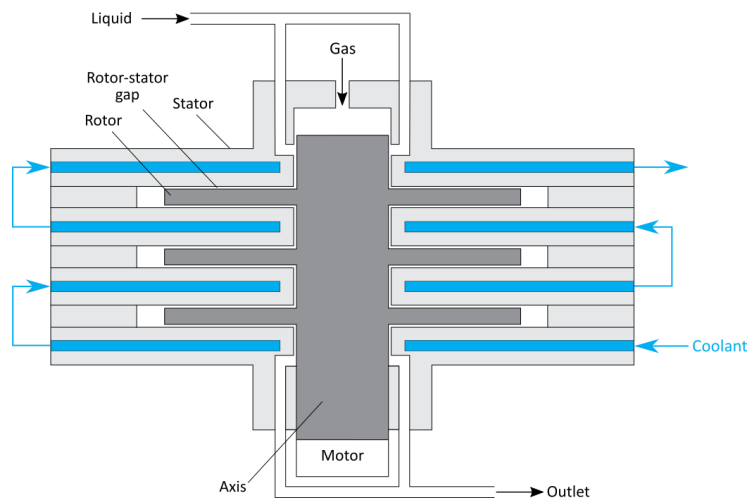


Figure 1. Sketch of a stirring disc reactor. [1]

The discs operate as impellers and rotate at high frequencies. The reaction volume flows around the rotating discs in a narrow channel to ensure a high contact area. High shear forces are applied to the reaction medium and the mixing of comparatively viscous fluids with low viscous monomers is possible. This SDR has three stages to obtain a higher reactor volume, and therefore higher throughput, which retains the power input at a reasonable level. The heat removal is realized via cooling channels inside the stator part of the reactor. SDRs can either be used as the main reactor for the polymerization or as a recycle reactor for a CSTR in which the main part of the polymerization takes place. Multiphase copolymerizations can be carried out as well on account of the high mass transfer rates and good heat removal capability.[1]

Since the design parameters are crucial for the mass and heat transfer inside the reactor, the SDR is simulated before manufacturing it to find the optimal conditions for polymerization reactions. In this work, the software Comsol Multiphysics® is used to conduct the simulations concerning momentum, heat and mass transfer. The variation of the geometry is investigated as well as the influence of the fluid properties. The heat transfer is examined depending on the used cooling medium and flow rates. All outcomes of the simulation are validated with existing experimental and simulated data to ensure reliable results.

Overall result: Overall, a SDR has been designed based on spatial aspects and species properties to obtain improved conditions for successful polymerizations involving high viscosities. Polymerizations in bulk or multiphase regimes can be executed with this reactor type.

Key words: Reactor design, viscous media, multiphase systems

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Your notes:

Implementation of Compartmentation in Kinetic LDPE-Models to Describe Mixing Effects in the Reaction Network

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With a market share of more than 17 %, low-density polyethylene is one of the most important plastics in the world. [1] Produced under high pressure from 1300 to 3500 bar and temperatures up to 300 °C, the polymeric structure effects its processing properties. Besides the reaction conditions, the choice of the reactor plays a big role in these properties. Despite the higher productivity of tubular reactors, LDPE produced in autoclave reactors has an important application in extrusion coating due to its unique tree like molecule structure and wide molecular weight distribution. [2] In many cases, chemical processes can be described with the model of a continuous stirred-tank reactor, but for high reaction rates with strong temperature-sensitivities, mixing effects have to be considered. While temperature profiles and concentration gradients of tubular reactors in simulation models can be described with plug flow, compartmentalized models are necessary for autoclave reactors.

To describe mixing effects for the free radical polymerisation of ethylene in a 100 ml stirred mini-plant reactor, a compartmentalized kinetic model based on the work of G. Wells is used. [3] For this, a cascade of multiple CSTRs, used as segments, describe the inlet of the reactor as a plume and backstreams represents the mixing of the hot reaction mass with the cold feed gas. Figure 1 shows the conjunction of the segments in the kinetic model.

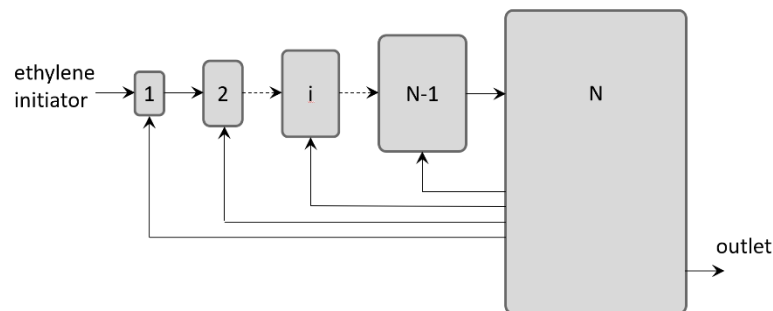


Figure 1: Scheme of the implemented segmentation in the kinetic model.

Each segment is described by the mass- and heat balance of a CSTR. The transfer of mass and heat between the segments takes place by convection whereas thermal conduction and diffusion is neglected due to the high flow rates.

The size of the segments is rising with increasing segment number to describe the growing and eroding injection plume. In segment one, the premixed feed gas of ethylene and an initiator is supplied and streams from segment to segment into the main reaction mass represented by the last segment. The erosion of the injection plume itself is described by flow streams from the main reaction mass in each previous segment.

With this model, the influence of back mixing and the use of different initiators were examined regarding the temperature profile and concentration gradients in the reactor as well as the molecular weight distribution and the chain densities of the formed polymer. Independent of the back mixing and the used initiator, the initiator concentration decreases along the injection plume due to its decomposition, but the low temperature initiator decomposes closer to the reactor inlet resulting in a narrower temperature gradient. This trend can also be seen in the radical concentration profile, shifting its maximum closer to the inlet. By a faster decomposition closer to the reactor inlet of the low temperature initiator, the effective reaction volume is smaller, leading to a smaller number average molecular weight and a smaller poly dispersity index. Also, a higher density of long chain branches can be seen for this initiator.

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Your notes:

Synthesis of polypropylene for 3D-printing applications

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3D-printing offers an alternative way to give plastics shape. In recent times this technology has made great progress and is used to generate prototype models or even small series products. Among existing technologies (e.g. Stereolithography, Selective Laser Sintering) the Fused Filament Fabrication (FFF) shows the highest potential for professional application and garage engineering. This method uses a thermoplastic material in the form of a filament. The material is molten and extruded through a moveable printer head that allows to fabricate objects layer-by-layer. While common materials for FFF are acrylonitrile butadiene styrene (ABS) and polylactic acid (PLA), polyolefins show potential for better mechanical properties [1].

To develop a polypropylene filament suitable for FFF, commercial materials were analysed first to find out the most important properties regarding printability. The most crucial properties that have been identified and should be optimized are crystallinity, molecular weight, dispersity and viscosity. The next step was the synthesis of polypropylene grades using an inhouse 0.5 L reactor, a high throughput system that enables multiple experiments per day. For polymerization an industrial Ziegler-Natta catalyst system was screened for the influence of H₂ partial pressure and the concentration of an external donor. A further series of experiments investigated the effect of different comonomers and their concentrations. The experimental plan was set up with the help of "Design-Expert" in order to uncover the factor interactions and define a mathematical model of the design space.

Five factors were investigated, therefore the resulting materials differed greatly in their properties. The presented work shows that with the help of statistical tools it is possible to find out optimal conditions that could result in printable polypropylene grades.

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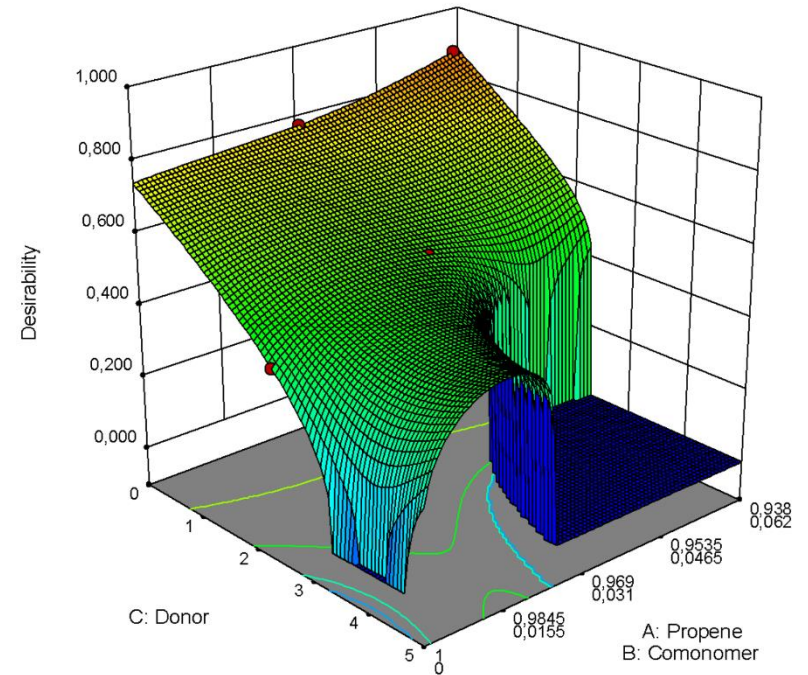


Figure 1 The results of the experimental design can identify factor combinations that give the desired material.

Heat transfer effects in the gas phase polymerization of propylene

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Polypropylene (PP) is a versatile polymeric material, which is used for many high-volume applications such as consumer goods, packaging, automotive parts and medical products. With a global market share of about 20%, PP is one of the most commercially important polymers. Industrially, heterogeneous Ziegler-Natta (ZN) catalysts are predominantly used for the polymerization of propylene. The catalyst greatly defines the physical properties of the final product as well as the productivity of the process. Since the development of ZN catalysts in the early 1950s, continuous improvements were performed with regard to higher catalyst activity and better product performance.

Modern, highly active ZN catalysts tend to increase problems associated with heat removal – in particular in the gas phase polymerization of propylene. Not only on the reactor scale in terms of meltdown or thermal runaway, but specifically on the particle scale. Especially at the polymerization start, when the pure catalyst shows maximum activity, particle overheating and/or uncontrolled catalyst fragmentation may occur. Due to the thermal sensitivity of the catalyst, active sites will be destroyed by overheating reducing the overall activity of the polymerization. Thus, the full activity potential of the catalyst may not be exploited. Furthermore, bad particle morphology may result leading to poor product quality.

The current contribution deals with the experimental and modelling study on heat transfer effects in the gas phase polymerization of propylene. Polymerization experiments were conducted with commercial ZN catalysts under industrial relevant conditions in a 5 L stirred tank gas phase reactor. The reactor was operated in semi-batch mode enabling to monitor the reaction rate under constant pressure and temperature. Experiments were performed under various conditions. Experimental results show that in the presence of a seed bed, the catalyst activity was increased much likely to an improved heat transfer between the growing polymer particles and its surrounding. To analyze and better understand the observed effects, a model with emphasis on process kinetics and particle overheating was developed. A crucial parameter is the heat transfer coefficient for which different literature correlations were considered.

Your notes:

Continuous solution polymerization as a tool for metallocene catalyzed homo- and co-polymerization investigation

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With a turnover of around 350 billion Euros per year plastics play an important role in European economy. Around one third of it can be addressed to polyethylene, being one of the most versatile products due to its broad range of possible properties. [1] Its physical specifics and processability strongly depend on the respective polymeric microstructure. As polyethylene only consists of hydrocarbons, the microstructure is given by short chain branches (SCB) in LDPE (Low Density Polyethylene) and LLDPE (Linear Low Density Polyethylene) and long chain branches (LCB) in LDPE. Thus HDPE (High Density Polyethylene) shows nearly no SCB's or LCB's and can be used wherever chemically and mechanically stable plastics are needed e.g. for pipes or milk bottles. HDPE as well as LLDPE are produced in solution using catalysts at moderate pressure (10-200 bar) and temperature (70-300°C) conditions and are similar on the microstructure scale. The difference is given by SCB's present in LLDPE and not in HDPE. On the macromolecular scale the difference is huge, as LLDPE is a very flexible and stable product which is often used in packaging but also wherever flexibility is needed e.g. for bearings or sealings. The product properties can easily be shifted from stable HDPE to flexible LLDPE by adding α -olefines as co-monomer. Each time the co-monomer is added to the backbone an SCB is produced lowering the crystallinity and density of the produced product. Here the combination of metallocenes and borate-salts showed very good productivity at nearly stoichiometric ratios. The homo-polymerization of ethene using metallocenes and borate-salts is well described in literature. Regarding co-polymerization batch and semi-batch investigations were already performed. [2] Through the changing ratio of co-monomer during the polymerization process, the resulting polymer properties cannot directly be correlated to the reaction conditions. Also kinetics can hardly be described in detail using this reaction regime.

To investigate the polymerization process under steady conditions a new continuous solution polymerization mini-plant was assembled. By this characteristics of the product and the polymerization process not accessible under batch or semi-batch conditions can be investigated now. Here each component can be fed separately. Adjustments regarding each monomer, scavenger or the metallocene/borate ratio can be done stepwise to determine the impact respectively. A calorimetric approach is used to determine the conversion online and by this it is possible to keep the monomer concentration at the same level at different process conditions. The polymer is analyzed using GPC connected to IR to determine molecular weight resolved co-monomer content for each sample and sequence length distributions using NMR.

Using this mini-plant samples with homogeneous comonomer content along the molecular weight distribution were produced and analyzed regarding the impact of the co-monomer on the catalyst performance and product properties. Also a comparison of continuously produced homo-polymerization product to literature known product obtained under semi-batch conditions using the same metallocene is now possible using the continuous mini-plant.

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Your notes:

Sorption equilibria relevant for catalytic olefin polymerization

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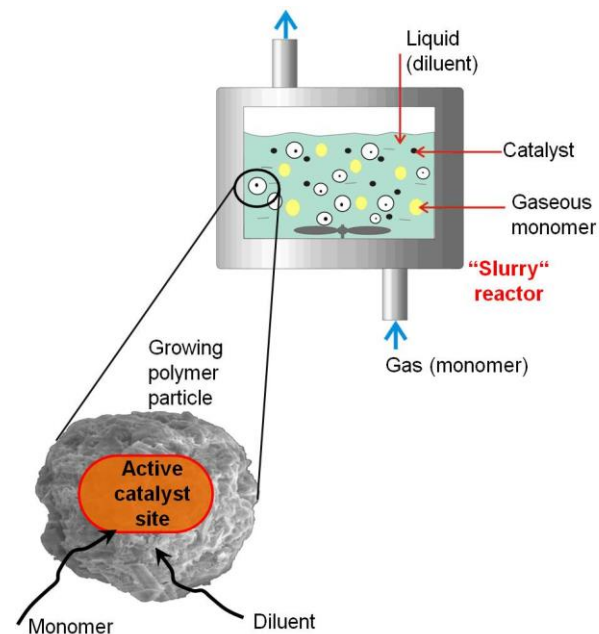
There are many reasons why the knowledge of phase equilibria during the catalytic olefin polymerization is important and why many researches are interested in exploring them. In any type of catalytic polymerization (solution, slurry, gas-phase) the proportional relation of the monomer concentration at the active catalyst site to the polymerization rate is essential. Phase equilibria for solvent, monomer(s), co-monomer(s) and polymer are important not only for the polymerization kinetics itself, but also for copolymer structure/composition. Subsequent product degassing is also closely related to sorption and diffusion in polyolefins. Nowadays many experimental techniques are available (e.g. DSC with pressure cell, low-field NMR, co sorption balances), thus the thermodynamics of polyolefins is persistently studied and a lot of new quantitative knowledge about polyolefin thermodynamics was accumulated. But still there is a need for new data required for some production processes and polyolefin grades.

The solubility and diffusion of monomer in the diluent is crucial when performing solution polymerization. Moreover, there are arguments and experimental evidence, that mass transport limitation through the polymer layer surrounding the catalyst is possible even at solution conditions.

In the case of slurry polymerization, liquid diluent is present in the reactor to improve heat removal. Polymer particles are swollen by the diluent and thus the monomer diffusion is hindered. The (co-)sorption and (co-)swelling equilibria of polymer-diluent-monomer are then desirable. Usually some co-monomers (e.g. 1-hexene, octane) are added to the reactor and their insertion into the polymer chain affects the copolymer product structure/composition.

During the gas-dispersion polymerization, monomer is dispersed in gaseous diluent (eventually co-solvent) and passes through the solid polymer particle and again (co-)sorption and (co-)swelling thermodynamics of polymer-solvent-monomer is required.

In this contribution we present data relevant for gas-phase and slurry polymerizations, i.e., sorption and swelling equilibria in polymer-gas and polymer-liquid systems, respectively. We measured sorption equilibria for gaseous (ethylene, propylene, 1-hexene) and liquid (hexane, pentane, octane) hydrocarbons in polyolefin samples. Our experimental results include sorption data for various polyethylenes and polypropylenes (covering the full spectrum of commercially produced grades) at different temperatures (relevant to polymerization conditions).



Furthermore, we compare our experimental data with advanced equation of state (PC-SAFT) predictions and they are in a good agreement. Our results from liquid sorption experiments of polyethylene/n-hexane system support the new morphological model of free and constrained amorphous phase in polyethylene introduced by Chmelař et al. (2015) [1].

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Your notes:

Thermodynamics effects on the reaction rate in gas phase polyolefin reactions

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Polyolefins include different types of polymers with a variety of properties. In terms of production volume, the most common thermoplastic used nowadays is polyethylene (PE). The global demand for this polymer is estimated to reach 99.6 million metric tons in 2018. The polymerization of ethylene on supported catalysts in gas phase fluidized bed reactors (FBRs) is the process of choice at the industrial scale, especially for linear low density polyethylene (LLDPE) production [1]. Gas phase processes are clean and less energy consuming. Yet, they have lower heat transfer capacity, which necessitates to limit their productivity. In order to improve heat transfer in gas processes, the “condensed operating mode” can be operated, where liquid species such as isobutene or n-hexane are injected together with the monomer feed into the reactor. These species can be referenced to as induced condensing agents (ICAs). The heat of vaporization absorbs a significant amount of the reaction heat. However, despite the wide-spread use of the condensed operating mode, very little is known about the impact of the ICAs on the solubility of ethylene in the polymer phase, and thus on the reaction rate and the production safety. Understanding the effect of ICA becomes essential in grade transition operations.

In the present study, we investigate the potential effect of the ICAs used in condensed mode operation on the solubility of ethylene in the polymer phase and consequently on the reaction rate. A combined kinetic and thermodynamic model of this process in a fluidized-bed reactor is proposed. The thermodynamic model is based on the Sanchez-Lacombe equation of state (SL EoS), which was found to have excellent predictive capabilities in the polymer domain [2]. This model is used in order to estimate the concentrations of ethylene and ICA in the amorphous polymer phase, either in the absence of an ICA (binary system) or in presence of ICA (ternary system). The predictions of the thermodynamic model are compared to experimental data obtained from open literature and good agreement is obtained. This model was found to give more precise data compared to Henry's law of solubility. The kinetic model is developed to describe the ethylene homopolymerization over Ziegler-Natta catalysts of one active site. The process model, is a dynamic FBR model approximated by a single-phase continuous stirred tank reactor within perfect mixing in the bed. The model assumes no mass and heat transfer resistance between the polymer particle and the gas phase. This model also includes the energy balance for the reaction mixture in the bed.

By incorporating the thermodynamic model in the process model, we show its predictive capabilities including the prediction of the effect of ICA on parameters such as production rate, reactor temperature and the concentration of different species inside the reactor. The predicted concentration of ethylene in the polymer particles are used in the kinetic model to calculate the reaction rate, rather than using the gas phase concentration, or using an approximation by Henry's law that does not account for the ICA effect. It is shown that the ICA can lead to an increase in the production rates. These observations were validated with experimental data from the literature, and were found to support previous results in our group [3]. The proposed model is expected to be a powerful tool for fundamental understanding of gas-phase polyolefin polymerization, and can be used in order to propose optimal grade transition strategies, with minimized waste and energy consumption during the transition.

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Your notes:

Sorption of liquid in polyethylene measured by low-field NMR

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Reaction rate in liquid-dispersion catalytic polymerization reactors and properties of the final product are influenced, among other phenomena, by a sorption of liquid diluent into polymer. The dynamics of such a liquid sorption is our focus as well as possible subsequent polymer morphological changes during the sorption. Our results primarily improve quantitative understanding of thermodynamics in the system of polyolefin with liquid diluent and may contribute to optimization of production processes.

As a model system, we consider the sorption of liquid n-hexane into polyethylene. Polyethylene contains two easily distinguishable phases: rigid and amorphous. Rigid phase is formed by a crystalline phase (30-70 wt.% of the sample) and an interphase (max 5 wt.% of the sample). As our data confirms, crystalline phase is inert to the sorption and the effect of the interphase on the sorption is supposed to be negligible for our purposes. The novel picture of amorphous phase containing constrained and free-amorphous components based on comprehensive experimental evidence was presented in [1]. Only the amorphous phase (i.e., both constrained and free-amorphous components) absorbs liquids or gases and changes accordingly its mobility and mass. These changes are easily measured by a low-field nuclear magnetic resonance, which is also known as time-domain NMR (TD-NMR).

TD-NMR has a high potential for a broad area of applications. For example, it is already successfully employed in the quantitative analysis of water content in fat or crude oil. Moreover, the speed of its measurement meets the requirements for utilizing it as an online sensor. Therefore, we decided to test its capabilities for measuring the liquid sorption dynamics.

To observe the sorption of liquid into polyethylene and the associated morphological changes, we utilized several measuring pulse sequences including Solid Echo pulse sequence (SE) and the evaluation procedure using multi-exponential curve fitting with one Gaussian fitting parameter. The SE can be optimized to detect components with short relaxation times even shorter than 15 μs (in our case rigid phase) and can simultaneously provide reliable data for components with long relaxation times.

Our NMR measurements with a range of polyethylene samples with different densities confirmed that the rigid phase of PE is really without any mobility or mass changes at the beginning of the sorption process and only the amorphous phase evolves. Moreover, for each PE sample, we were able to evaluate the amount of solvent that diffuses into amorphous phase during the sorption and thus to construct time dependencies of the liquid sorption. We were also able to characterize desorption process and found that there is no hysteresis in sorption/desorption behavior. Changes of relaxation times in hexane-swollen amorphous phase in dependence on conditions are important for the fundamental understanding of diffusion in polyolefins.

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Your notes:

Design and characterization of a gas-solid reaction calorimeter

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The IUPAC Gold Book defines calorimetry as “...any experiment in which heat is measured as some chemical reaction or physical process occurs”[1]. This is true for the earliest ice calorimeter designed by Lavoisier, as well as for the wide spectrum of modern applications like real time reaction calorimeters, bomb or micro calorimeters, etc. One of the main issues of calorimetry has always been the safety of chemical processes, especially in industrial scale[2,3]. For example, magnitudes of interest are the gross heat of reactions or the adiabatic increase in temperature[4]. Despite the wide range of applications in the technology of calorimeters, it is extremely challenging to investigate reactions between solids/ highly viscous reagents and gases.

In order to address this problem, a gas-solid reaction calorimeter has been designed and realized. Essentially, it is a modified and insulated semi batch rotary pipe reactor (Fig. 1). By means of the design, the heat can be measured via heat balance, solids can be continuously mixed and gas can be simultaneously dosed. The cylindrical reactor consists of a reaction chamber (1) a cavity (2) and a rotating shaft (3) which allows the reactor to rotate. A further cavity (2) is also implemented in the lid and in the jacket of the reactor. The cavities can be evacuated in order to minimize heat loss to the environment. In combination with the reactor the jacket forms an annular gap (4). During a reaction a tempering medium flows through the gap and transports heat out of the reactor. By measuring the temperature at the inlet/outlet and considering the mass flow, the released heat can be calculated. Furthermore, the rotation of the reactor leads to a specific flow pattern in the gap (Taylor vortices) which facilitates the uniform flow with reduced backmixing. In order to hold the reactor in position and to avoid leaks, the jacket contains two ball bearing and two radial shaft sealings connected to a flange (6).

The flow regime was characterized by a design of experiments. The aim was to vary the influencing parameters (flow rate, rotational speed and incline) in order to obtain high Bodenstein Numbers. Furthermore, experiments were conducted to ensure optimal mixing for solids during reactions. A specially designed lid with an integrated heating element, suitable for constant rotation, was designed and used in order to calibrate the calorimeter. Finally, gas-solid reactions were performed.

As a result the suitability of the reactor for calorimetric measurements was confirmed. Further-more, the precision and the accuracy of the system were quantified.

In future research, chemical processes, which have not been properly investigated by calorimetric techniques due to a lack of adequate measurement systems, will be focused on. That includes especially polymerizations of industrial interest. One example might be the ionic polymerization of alkali cellulose with ethylene oxide, which leads to a decades old industrial product of yet unknown reaction enthalpy.

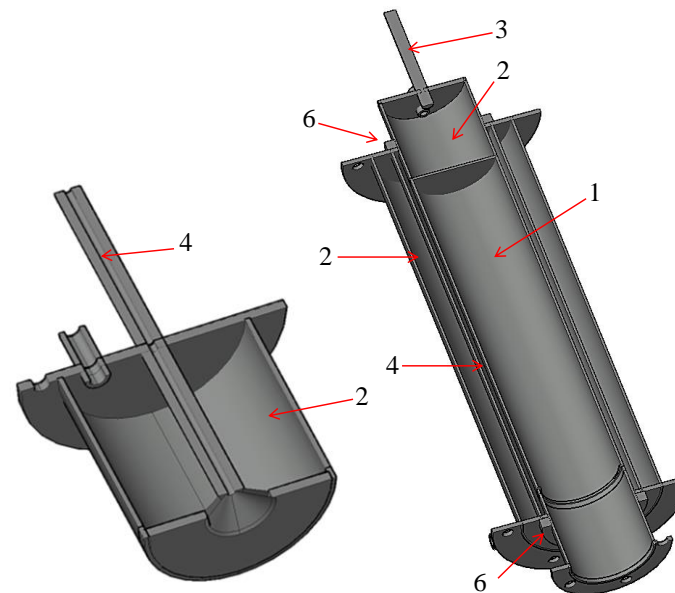


Fig. 1: Schematic representation of the gas-solid reaction calorimeter.

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Abstract Polymerizations usually come along with heat development during the reaction and some of those were extremely exothermic reactions, which were difficult to control in terms of safety reaction conditions. In those extremely exothermic reactions, the heat removal is one of the limiting factors in the design of chemical industrial scale production plants for a safe production process. Micro- reaction or –process engineering offers a technology for the development of new ways to design those production plants. Due to the high surface to volume ratio, the heat removal of micro reactors is highly increased in comparison to standard reaction vessels. Furthermore, highly exothermic and under normal conditions explosive reactions can be handled safely in micro reactors. In addition, micro reaction engineering offers a fast and low risk way for the scale-up from lab to production plants. The patented Miprowa® Technology by EHRFELD MIKROTECHNIK is a promising technology for micro reactors in industrial production scale. The Miprowa® Technology combines the benefits of a defined rectangular channel with dimensions in the lower millimeter range and planar static mixing inserts.^[1]

In this work, the Miprowa® Lab reactor was characterized in terms of pressure drop and heat transfer for different planar static mixing inserts. The Miprowa® Lab reactor consists of eight rectangular channels (each 12x1.5x300 mm), which can be fitted with different static mixing inserts. A typical static mixing insert and the Miprowa® Lab reactor are shown in Figure 1, we used mixing inserts with 30° and 45° angle. Furthermore, the temperature and pressure were analyzed in-line with a Lab-View/LabVision program.

The pressure drop in the reaction channel was determined for different mixing inserts and different process media. Those results were compared to CFD-simulations. Furthermore, the heat transfer between process and service fluid determined. In addition, the influence of the inserts on the pressure drop and the heat transfer were evaluated. The influence of the temperature, the mass flow in the reactor shell as well as the mass flow through the reaction channel and of the viscosity of the process and service fluid on the heat transfer were determined.

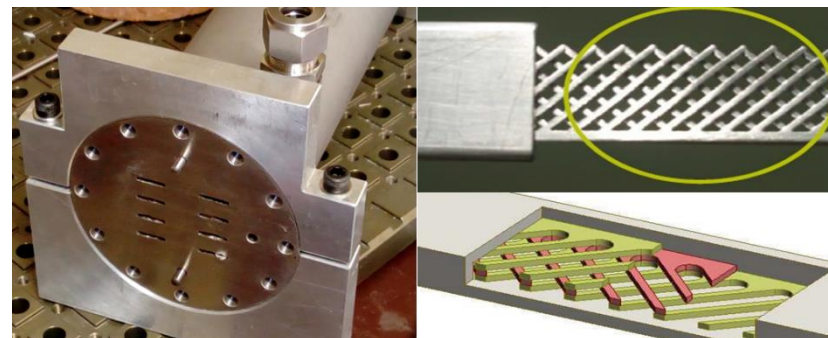


Figure 1: Left: Miprowa® Lab reactor with 8 rectangular channels. Right: Static mixing inserts and a schematic view the channel with mixing inserts.^[1]

In the future, these results should be used to validate a model for the Miprowa® Lab reactor as well for the production scale channels of the Miprowa® Matrix reactor.

Keywords: heat transfer, pressure drop, micro reactor, static mixing chamber, easy scale up, numbering up, high surface/volume ratio

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Modeling of Ethyl Linoleate Polymerization for Better Understanding of the Drying Process of Oil Paint

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Complex polymerization problems arise in the field of restoration and conservation of art. Many paints and coatings consist of triacylglycerides (TAG) that polymerize and form hard films at the room temperature and atmospheric pressure. These films are known to be unstable within decades and centuries. Our starting point to explore this process is to model polymerization of ethyl linoleate (EL), which follows reaction pathways similar to the TAG molecule. This polymerization is not trivial and cannot be treated by means of existing polymer reaction engineering approaches.

EL undergoes series of transformations before it even starts polymerizing and forms 3 types of crosslinks with other monomers¹. Due to the complexity of the monomer structure we face a combinatorial explosion of the number of states of one EL unit outside and within the polymer network. For this purpose we developed a methodology based on so-called 'monomer approach'. In this approach we do not consider the chain formation explicitly, but rather keep statistics over the basic units that form polymer network. The number of molecular species scales down from infinity to the number of unique fragments that contribute to the network. We developed an automated reaction mechanism² that reconstructs all possible configurations of these fragments and captures all possible reactions between them in a form of a reaction network. This reaction network is then transformed into the population balance equations. Solving them, we obtain the distribution of crosslinks over the drying time of EL. Applying random graph theory, this information can be used further to uncover properties of the polymer network, such as predicting gel point and obtaining molecular weight distribution. This methodology is generic and can be applied to other complex polymerization problems.

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Your notes:

Evaluation and synthesis of chemical blowing agents for the development of light weight acrylate-based 3D printing inks

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The PolyJet Technology is a common used 3D printing technology, able to produce complex and precise products [1]. The printed product is built up of numerous thin layers of an acrylic based ink system. In order to further improve the properties of the ink system in terms of weight reduction, a foamable ink is developed in which the thin layers are expanded prior to curing. This creates a cellular structure in the product, which offers numerous advantages.

The aim of the presented work is the development of a chemical blowing agent (BA), which is suitable for the application in an acrylate-based 3D printer ink. Initial evaluations of commercial blowing agents were unsatisfactory concerning the stability in the ink matrix. In order to solve this problem, various attempts are made to prevent the premature decomposition of the blowing agent. Unfortunately, it was not possible to find a suitable commercial blowing agent. Therefore, new functionalized sulfonyl hydrazide-based blowing agents are being developed. The developed blowing agents retain the foaming performance and show significant improvements in chemical stability in various thermal analyses compared to the commercial sulfonyl hydrazide-based blowing agents (Figure 1). Initial printing trials of the ink blends with the newly developed blowing agents show good printability since thin layers can be printed, subsequently foamed and cured.

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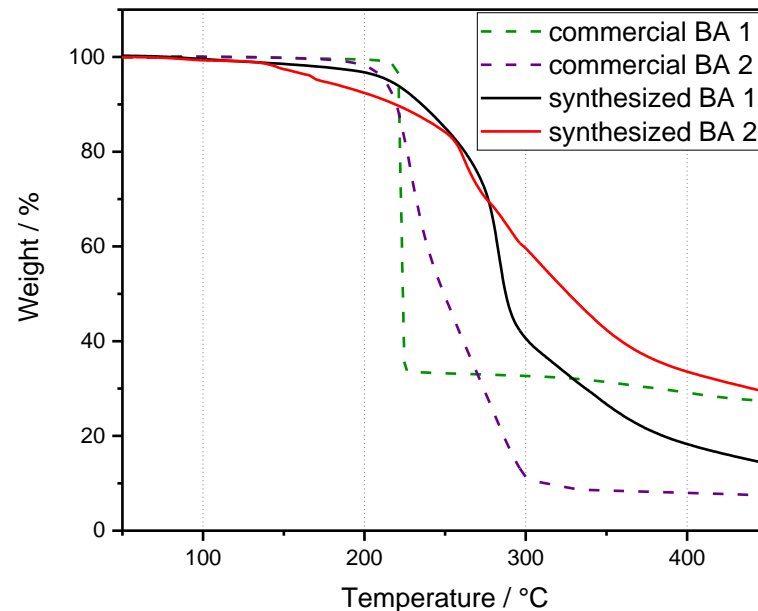


Figure 1: Comparison of the TGA analysis of commercial and new synthesized BAs.

References:

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A NEW APPROACH TO STOPPED-FLOW REACTIONS FOR SLURRY AND GAS-PHASE OLEFIN
POLYMERIZATION

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Given the industrial relevance of polyolefin production, it is certainly of great interest to understand the phenomena taking place during the reaction start-up. The first few seconds, or fractions of a second, are a determining moment in which morphology formation takes place and where the risk of particle overheating is at its highest. Nevertheless, the main drawback to studying these early stages is the lack of adapted apparatus that allow collecting accurate experimental data. It is, therefore, useful to have specifically designed tools for different processes. In this work, a combined approach of slurry and gas-phase systems was taken to evaluate the initial conditions of catalyst treatment for nascent olefin polymerization in supported catalysts.

A rapid-quench slurry system was set up to perform polymerization reactions. Unlike previous works¹, in which the stopped-flow technique was applied using separate vessels interconnected by tubes, our set-up was conceived in a single vessel under mechanical agitation and the reaction quenching was done by pressurized CO₂.

In parallel, a new stopped-flow gas-phase reactor has been developed for olefin polymerization, aiming to improve certain aspects of previous versions developed over the past few years in the C2P2 lab²⁻⁵. Our aims were to increase the polymer production capacity and reduce risks of temperature gradients formation inside the reactor, allowing for more accurate kinetic studies in the nascent polymerization phase. A solid porous membrane was incorporated inside the reactor, aiming to improve the gas convection and reduce the possibility of temperature gradients inside the reactor.

The main goal of this study was to compare the impact of initial conditions of catalyst treatment in slurry and gas-phase under industrially relevant conditions and collect experimental data on important phenomena such as catalyst fragmentation and particle morphology development. Following steps include building up a physical interpretation of the impact of the startup conditions on initial particle overheating, reaction rate and morphology (fragmentation).

Your notes:

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Polymerization kinetics of Ziegler-Natta PP catalysts

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In this study, a screening of different parameters on the activity of 4 given Ziegler-Natta catalysts was performed for a simple slurry polymerization of propylene. For the screening, a 0.5 L reactor equipped with an internal heating system was used. The internal heating system is able to control the set temperature through a compensating heating method. That way, the temperature is kept constant and only the power (measured in [W] or [%]) reacts to different influences which would change the temperature. By keeping the jacket heating of the reactor about 5 °C lower than the wanted polymerization temperature, the temperature is fully controlled by the additional heating of the internal heating up the reactor. By keeping track of the power of the internal heating, exothermal changes on the temperature such as the heat of polymerization can be observed. So when during the polymerization exothermal heat is produced, the internal heating will react to that by lowering the power to keep up the set temperature. By doing so, it is possible to record the whole activity curve of the catalyst throughout the polymerization.

Over the course of this study, 4 different Ziegler-Natta catalysts (4th generation) were characterized through screening of different influential parameters on their respective activity curves. The varied parameters observed were hydrogen amount as well as polymerization temperature. Each catalyst was tested at 3 different polymerization temperatures (70, 80 and 90 °C) and 3 different hydrogen amounts (low, center and high point). Through the internal heating and the change in the compensating heating power, effects on the activity as well as kinetics throughout the polymerization were observed and documented. With the compensating heating power curve obtained, kinetic parameters such as activation, propagation and deactivation can be fitted using an estimating mathematical fitting model for those kinetic parameters. Those parameters help revealing the catalyst reaction performance as well as help characterizing the catalysts activity profile. In **Figure 1**, a curve illustrating the typical power level change of the internal heating is shown. [1]

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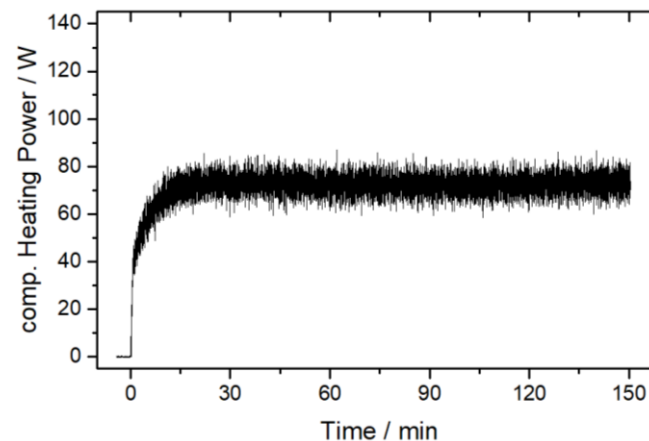


Figure 1: Typical power level curve of the internal heating over the course of a simple slurry polymerization.

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Effect of hydrogen partitioning on Homo-Propylene Polymerization Kinetics

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Key words: Homo-Propylene, Bulk Polymerization, Kinetics, Hydrogen partitioning

Despite the intense amount of research to improve the performance, efficiency and costs of polypropylene production, scale up of the scientific results from laboratory scale batch reactors to industrial scale continuous production plants remains still a challenge. In order to illustrate effects of scale-up in terms of kinetics, bulk phase syntheses of homo-polypropylene are presented for two grades with different melt flow rate (MFR) targets (50, 7.5 g/10mins) in different reactor sizes (0.25 and 5l) with calorimetric monitoring of the heat of reaction. In coordinative polymerization of propylene, molecular weight is mainly controlled by addition of hydrogen as chain transfer agent^[1]. In laboratory scale, bulk phase polymerization reactions are typically carried out in partially filled reactors. In such partially filled reactors, partitioning of hydrogen between gas phase and liquid phase takes place. In the used 5 liter reactor, for all MFR grades studied, uni-modal molecular weight distributions have been observed. In contrast in the 0.25 liters reactor, it was surprisingly observed, that high MFR grades show a bi-modality in molecular weight. In order to study this phenomenon, hydrogen concentration in liquid phase (x_{H_2}) has been investigated before and during the polymerization reaction by a combination of gas chromatography measurements and mass balance calculations. It could be shown, that in the 0.25 liter reactor, a drift in hydrogen concentration in the liquid phase is responsible for the observed bimodalities in molecular weight. Due to consumption of propylene, the hydrogen concentration is increasing during the course of reaction. A two-step feeding procedure for the 0.25 liter reactor has been developed in order to minimize these drifts in concentration. The developed procedure allows producing unimodal product also at high MFR grades. In addition, a correlation between the composition of materials in the reactor (z_{H_2}) and the concentration of hydrogen in the liquid phase has been established. This correlation has been used to design bimodal reactions in the 5 liter reactor. The experimental MFR results were in agreement with the targeted values.

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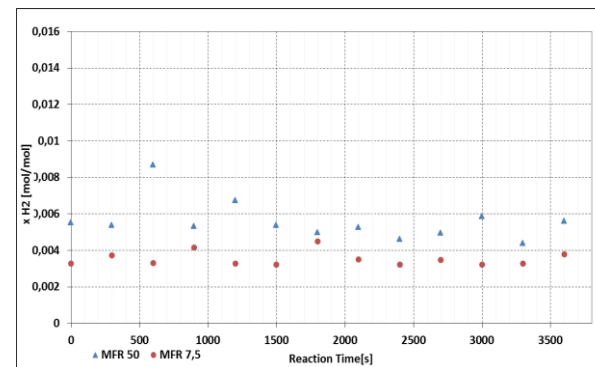


Figure 1: x_{H_2} during the reaction in the 5 liter reactor

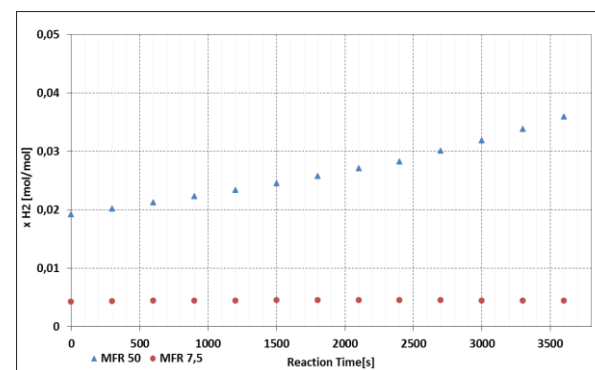


Figure 2: x_{H_2} during the reaction in the 0.25 liter reactor

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Impact of Condensing Agents in Different Temperatures in the Gas Phase Polymerization of Ethylene

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It is well known that chemically inert compounds, typically C₂ through C₆ alkanes are used in modern gas phase processes for ethylene polymerisation in order to improve the evacuation of heat producer during the production process, thereby allowing manufacturers to increase productivity. They can either be injected in vapour phase along with the monomer feed to help regulate partial pressures and to significantly improve the heat transfer capacity of the gas phase, or they can be (partially) liquefied in an external heat exchanger before being atomised at the entry to the reactor. In this second case, the reactor is said to be operating in “condensed mode”. Here, the dew point of the mixed vapor/liquid feed stream is adjusted so that it is below the reactor temperature. This means that (almost immediately) upon entering the reactor, the liquid droplets are vaporised. Thus, the heat removal is enhanced by both the latent heat of vaporisation of the alkanes, often referred to as Induced Condensing Agents (ICA), as well as their contribution to the heat capacity of the vapor phase.

Physical and chemical phenomena may occur at different particle and molecule level scales in the reactor. ICA can cause changes in solubility and physical properties, which may facilitate the transport of ethylene and hydrogen. In early stages of the reaction we are required to accurately describe the physical phenomena related to the sorption equilibrium of the monomer as well as other gas phase species for the polymer phase and their diffusion over the polymer phase to the active sites. The permeability of gaseous components occurs only in the amorphous phase of the polymer. This permeability is the result of the combination between the absorption equilibrium phenomena and the heat transfer and mass resistance. Prediction of permeability coefficients can only be achieved based on knowledge of the corresponding solubility and diffusivity coefficients.

A series of ethylene homopolymerizations in the presence of vaporized *n*-pentane and *n*-hexane were run at 70°C, 80°C and 90°C. It was found that the effect of temperature on the homopolymerization of ethylene in the presence of an ICA is not exactly what one might expect if the cosolubility effect is neglected. In fact, despite the fact that these polymerizations are highly exothermic reactions (hence the need for the ICA in the first place), increasing the reaction temperature from 70°C to 80°C to 90°C can actually lead to a decrease in the rate of polymerisation in the presence of large quantities of ICA (in the case of the homopolymerizations with no ICA, the effect was as expected).

This can be attributed to that the fact that while the propagation rate increases with temperature, the solubility of the ICA decreases. This latter change causes the concentration of ethylene in the amorphous phase of the polymer to be drop at 90°C with respect to 70°C. In certain cases, this decrease in ethylene concentration is more important that the increase in the propagation rate. The curves at 90°C do not express the co-solubility effect. This is because a concentration of monomer in amorphous phase is also associated with heat transfer in simple particle.

Key Words: Polyethylene in gas phase, Induced Condensing Agents, Cosolubility effect; Heat transfer.

Your notes:

Experimental and Modeling Study of Ethylene Polymerization in Gas Phase Reactors

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Polyethylene is by far the most significant polymer worldwide in terms of volume of production, and demand for this product continues to rise. This means that producers need to increase capacity either by improving existing processes, or building newer, more efficient processes. For gas phase processes, which represent nearly 50% of all production processes, fluidized bed reactors are the equipment of choice at the industrial scale. One of the major operational issues associated with increasing capacity in gas phase reactors is the ability to remove the significant amount of heat produced during the reaction. A popular approach to control overheating is the so-called “condensed operating mode” where liquid species are injected together with the monomer feed [1]. Upon entering the reactor, the liquefied components vaporize and the latent heat of evaporation helps to cool the system. However, it has recently been demonstrated that the inert species most typically used for this purpose can strongly influence the solubility of all species in the growing polymer particles [2].

Extensive literature search clearly shows that very little solubility data is available for ternary systems, let alone quaternary systems. However, modern polyethylene gas phase reactors reveals that the vapor phase can contain many condensable species (even as many as 7 or 8) that can lead to significant complexity in modelling sorption, as well as understand the solubility behavior. Positive experience using the Sanchez-Lacombe equation of state in the past motivates us to extend it to more realistic situations [3]. We will therefore build on our common past experience using chromatographic techniques to look at sorption/desorption of vapor mixtures from polyethylene powders and to identify model parameters from equilibrium sorption.

We aim to achieve this task through experiments in 2 liter stirred tank reactors. This reactor can be run under a range of pressures from atmospheric to 30 bars and under a range of temperature. An insoluble gas (e.g. Nitrogen or Argon) will be used to carefully measure the volume of the void space among the polymer particles and in the feed lines. Then, mixtures of soluble gases will be used to measure the solubility effect. Gas phase composition will be measured with an upgraded Micro GC capable of providing very rapid composition analyses from very small samples. The solubility data and the transport properties will be used to fit binary interaction parameters for the Sanchez-Lacombe equation of State, and for diffusion coefficients for different powders and gas mixtures (under pressure).

Finally, Differential Scanning Calorimetry will be also used to study the impact of the alkanes on the thermal properties, crystallinity, melting and melt onset temperatures of powders exposed to different mixtures of alkanes.

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Your notes:

Kinetics and product properties of the ethylene polymerization with five different bisimine pyridine iron catalysts

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Bisimine pyridine iron catalysts (BIP catalysts) are highly active iron-based catalysts for the ethylene polymerization. They are environmental friendly as well as cheap and easy to prepare. In combination with a cocatalyst such as methylaluminumoxan (MAO), it is possible to prepare HDPE with tunable chain length and end-group functionality. BIP catalysts enable the one-pot synthesis of hydroxyl terminated polyethylene, an ideal precursor for the preparation of diblock copolymers, which is very complex to prepare in other processes.

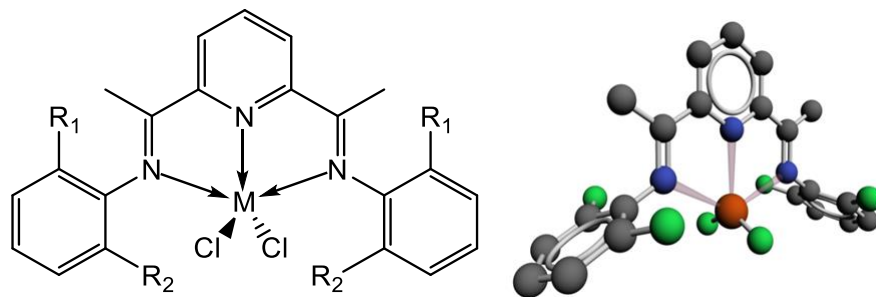


Figure 1. structure of bisimine pyridine catalysts.

For tailoring the product properties, it is important to understand the reaction in further depth and to gain deeper knowledge in the propagation mechanism. For this purpose, a kinetic study of the ethylene polymerization with five different BIP catalysts was performed. The results were then used to determine the mechanism of the chain propagation. The influence of steric and electronic properties of the ligands of the BIP catalysts on the polymerization were further investigated.

A first order rate law dependency of both, the monomer and the catalyst concentration was found. The cocatalyst was found to be uninvolved in the propagation step. The proposed propagation mechanism follows a typical *Cossée-Arlman* mechanism.

Your notes:

Modelling of a Solution Polymerization Mini-Plant

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Within the chemical industry, the plastic segments are one of the largest sale sectors. Polyolefins hold for more than 55 % of global plastics materials demand. Among polyolefins polyethylene (PE) has the highest turnover. [1] PE is divided into different types based on its densities that are given by the structural variations. In particular, the degree and length of the branching of the backbone influences the density and material properties. A common PE type is the linear low density PE (LLDPE) with only short chain branches. [2] Its characteristic structure results from the catalytic synthesis using ethene and an α -olefin as comonomer at pressures between 10 to 200 bar and temperatures up to 300 °C. LLDPE is mainly recovered by solvent, slurry or gas phase polymerization processes. [3] In order to investigate the solution polymerization an experimental mini-plant is used. To improve the experimental procedure, a model to determine the conversion online is developed. With it, the control of the reaction can be increased and thus the experimental effort can be reduced.

In general, the use of modelling in addition to experiments can be beneficial regarding time and costs due to reducing the necessary experimental expense. Especially in the sectors of product development and process optimization, modelling is a valuable tool. Further, it can improve the understanding of the investigated processes. For the stirred tank reactor of the LLDPE mini-plant a model for online determination of the conversion is developed based on the heat balance. The alternative gravimetrical method to determine the conversion requires several days and is therefore not suitable for an online application. The online determination allows the adjustment of the conversion during the experiments by changing the operation parameters. The heat balance for a continuous autoclave with a heating jacket consists of the heat input from the heating jacket, the heat loss to the surroundings, and the heat loss to the feed. [4] During the reaction, the polymerization heat is included in the heat balance whereby the amount of heat is depending on the conversion of ethene and comonomer. Further, an additional heat source is detected during the experiments at the LLDPE mini-plant. This heat source is assigned to heat produced by stirring due to experimental results in line with theoretical approaches. The amount of heat input from the stirrer depends on the composition of the solution, the synthesized polymer, and the operation parameters including pressure, temperature, and stirring speed. To reduce the complexity and number of correlations, the heat input of the stirrer is calibrated to the experimentally measured torque of the stirrer. With it, the additional heat source through stirring can be calculated for further experiments.

For the continuous stirred tank reactor of the LLDPE mini-plant the heat balance is successfully set up. At steady state conditions the polymerization heat and thus the conversion can be calculated online. Due to estimations used in the heat balance, the accuracy of the calculated online conversion depends strongly on the experimental conditions during the experiments used for the calibration compared to the experiments, where the heat balance is applied to determine the conversion online. Within the error range, requested conversions can be obtained by adjusting the operation parameters during experiments.

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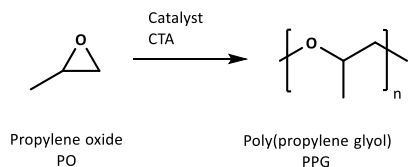
**A new and simple method to obtain easily and quickly kinetic and thermodynamic data via
online FTIR-spectroscopy**

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The knowledge of overall reaction rates of a process is of major interest and often crucial for reactor designing. Several methods are described in literature that allow determination of reaction rates [1] They have in common that they may be quite time-consuming, or are giving data that do not necessarily meet criteria of robustness or accuracy or disturb the reaction.[2,3] We will report upon a simple method that uses pulsed additions of monomer, here propylene oxide (PO), to obtain kinetic and thermodynamic data of the propagation step of a living polymerization.

Online FTIR-spectroscopy was used to monitor the concentration of monomer throughout the experiment using a partial least squares (PLS) regression model for multivariate data analysis that was previously set-up for the reaction system (Figure 1). The method was developed for kinetic studies of PO homopolymerization catalyzed by double metal cyanides (DMCs) (Scheme 1).



Scheme 1 Homopolymerization of PO to PPG.

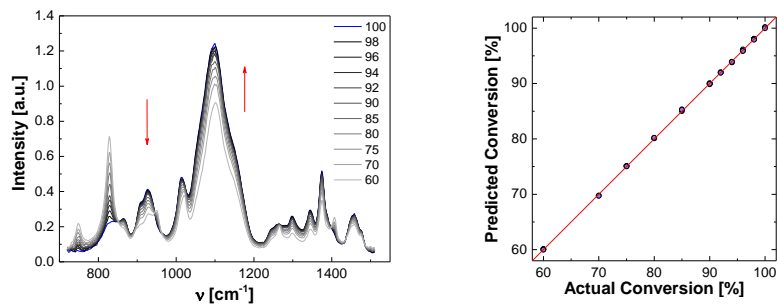


Figure 1 IR spectra of reaction system at different PO conversions (left) and PLS regression (right).

A certain amount of monomer was added with a relatively high feeding-rate into the autoclave that is charged with catalyst and chain transfer agent (e.g. low molecular weight PPG). Concentration of monomer at specific reaction times were calculated by using feeding rate, feeding time and conversion of PO that was received by previously mentioned FTIR measurements. The propagation reaction of the substantially immortal polymerization can be treated as pseudo-first order; plotting $\ln[\text{PO}]$ against reaction time gives a linear dependence. It allows determination of rate coefficient from the slope of linear regression.

The main advantage of this method is that for each feeding-step the reaction conditions, such as temperature, can be varied. Furthermore, the concentrations of catalyst as well as of endgroups changes throughout the experiment, so that one experiment produces many data points. This enables an evaluation along Arrhenius and/or Eyring theory after one experiment. In addition, the reaction rates can be plotted in dependence of temperature and concentration of endgroups. The visual representation of catalysts kinetic and thermal performance allows determination of optimal process conditions in terms of highest reaction rates and provides information on the thermal decomposition of catalytic species. The method therefore helps to identify optimal polymerization parameter.

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Your notes:

In-line Monitoring of growth of nano-scaled particles and droplets in concentrated liquid dispersions by photon density wave spectroscopy

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Photon Density Wave (PDW) spectroscopy determines the absolute optical properties of a turbid liquid material without a need for calibration. As it is applicable especially at highest turbidities [1], complex multiple light scattering materials can be investigated without dilution. This is of particular interest for particle sizing in materials which are prone to size changes during dilution. Common methods like dynamic or static light scattering require single scattering and hence dilution of the material under investigation. Furthermore, as PDW spectroscopy currently allows for a time resolution of approx. 2 min⁻¹ and can be operated with fiber-optical probes [2], it allows for in-line measurements during chemical, physical, or biological processing of turbid liquid materials. To date only a limited number of process analytical technologies, suitable for high concentrations of highly light scattering particles, exist. PDW spectroscopy [3-6] separately quantifies light absorption and light scattering in multiple scattering liquid dispersions of particles, droplets, or biological cells. Applicable in systems where the absorption coefficient μ_a is significantly smaller than the reduced scattering coefficient μ_s' , PDW spectroscopy can be applied to monitor optical changes of such dispersions and for sizing of the dispersed structures in the nano- and micrometer regime. The PDW spectrometer utilized here is self-built. Technical details can be found elsewhere [7].

Currently, techniques for in-line process monitoring in liquid dispersions are typically either hindered by the optical diffraction limit (e.g. video microscopy [8]), are restricted in the upper addressable particle concentration, and/or are biased by particle flow (e.g. diffusing wave spectroscopy or fiber-optical quasi-elastic light scattering [8-10]). However, for dispersions containing nano- or micrometer sized particles with volume fractions $\phi > 0.4$, PDW spectroscopy is one of the very few suitable techniques, yet widely unknown. It enables particle sizing in such highly concentrated dispersions in a diameter range of approx. 50 nm – 500 μm .

PDW spectroscopy is not based on sensing particle diffusion, but directly quantifies multiply scattered light instead. It therefore does not probe hydrodynamic particle properties and hence avoids problems arising from changes of (micro-)viscosities. The experimental absorption coefficient yields information about the chemical composition of the turbid material. The reduced scattering coefficient is, amongst others, linked to the diameter d of the scatterers. PDW spectroscopy was applied for the inline monitoring of polymerization processes like the synthesis of highly concentrated functionalized poly(vinyl acetate) adhesives. Using multiple laser wavelengths for PDW spectroscopy, an estimation of the particle size distribution during synthesis was obtained as well [11].

Nanoemulsions have become more and more important in recent years. An effective way for producing such droplets with a narrow size distribution is the phase inversion temperature (PIT) emulsification. In this example, varying emulsifier concentrations were used for the preparation of the nanoemulsions to investigate their influence on the Ostwald ripening rate. Accordingly, the amount of emulsifier has a large influence on the stability of the system. Ostwald ripening rates obtained inline by PDW spectroscopy were in good agreement with literature values. Here, PDW spectroscopy was applied to investigate the growth of polymer nanoparticles during their synthesis. Examples cover styrene homopolymerization, semi-batch polymerization of vinyl acetate, and starved feed copolymerization of acrylate-based monomers. Also, the stability of nanodroplets was investigated, deducing Ostwald ripening rates of nanodroplets after their formation [12].

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In-line monitoring of Phase Inversion Temperature polymerization of Styrene with Photon Density Wave spectroscopy and Particle Vision Microscopy

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Lately, process analysis is an important topic for many industrial applications, e.g., polymerization, cosmetics, dairy products, fermentation and all kinds of emulsification processes. The currently established measurement techniques are only able to address a small variety of these applications, since high concentrations and therefore highly light scattering and absorbing materials create difficult measurement conditions for most analytical techniques. Therefore, the requirement of dilution and, hence, off-line analysis often lead to false conclusions about the current state of the observed process or are too slow to use as a basis for making reactive changes to process conditions to achieve desired product characteristics.

Nowadays, a few new methods like Photon Density Wave (PDW) spectroscopy or Particle Vision Microscopy (PVM) try to address these challenges and offer an in-line possibility to answer crucial questions about processes such as particle self-assembly and growth. An important goal is to not only observe the reaction, but to model and control the processes.

To demonstrate the applicability of these Process Analytical Technologies, PDW spectroscopy and PVM were applied to investigate a Phase Inversion Temperature (PIT) polymerization of styrene, with a volume fraction of the monomer well above 30 %. The PIT method is commonly used to produce emulsions in the nanometer regime without the need of a high energy homogenization. Since the final nano-droplet size can be adjusted by the cooling rate during the PIT process, a subsequent polymerization of these droplets should allow for a different particle size regime in comparison to the conventional emulsion polymerization of styrene. [1] Using PDW spectroscopy it is possible to achieve in-line monitoring of particle size distribution under conditions of solid content and optical density which would otherwise limit the effectiveness of other analytical methods.

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