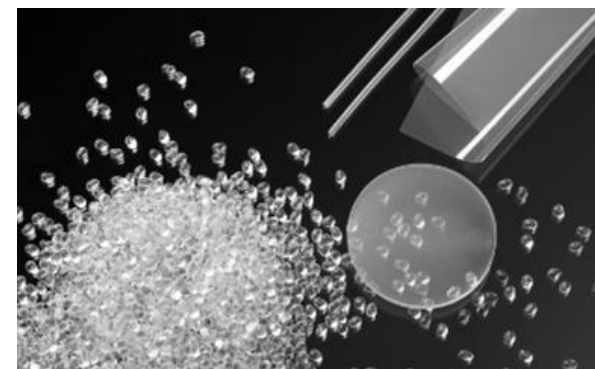
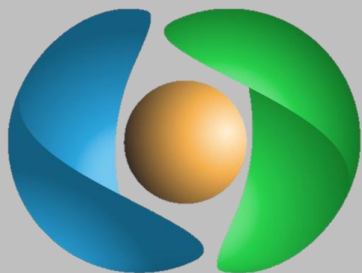


Conference Guide

8th PhD-Workshop on Polymer Reaction Engineering

14th June to 16th June 2019 in Hamburg





Welcome to the 8th 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 eighth 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 48 registrations in Prague. In this year we are expecting 47 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:

- process advancements 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: deterministic and stochastic
- focusing on structure-property relationships and thermodynamics

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

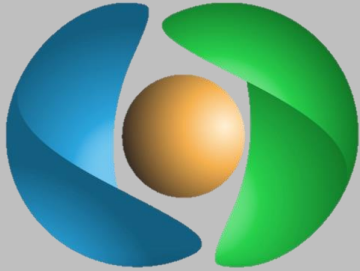
The Organizing Committee

Organizing Committee

Markus Busch	Chair of WPPRE, TU Darmstadt
Werner Pauer	Secretary of WPPRE, University of Hamburg
Paul Peikert	Technical University Darmstadt
Elisabeth Schulz	Technical University Darmstadt
Sarah-Franziska Stahl	University of Hamburg
Sebastian Eller	University of Hamburg

Sponsors





General Information

Language

The official language of 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 Germany is +49.

Emergency phone numbers

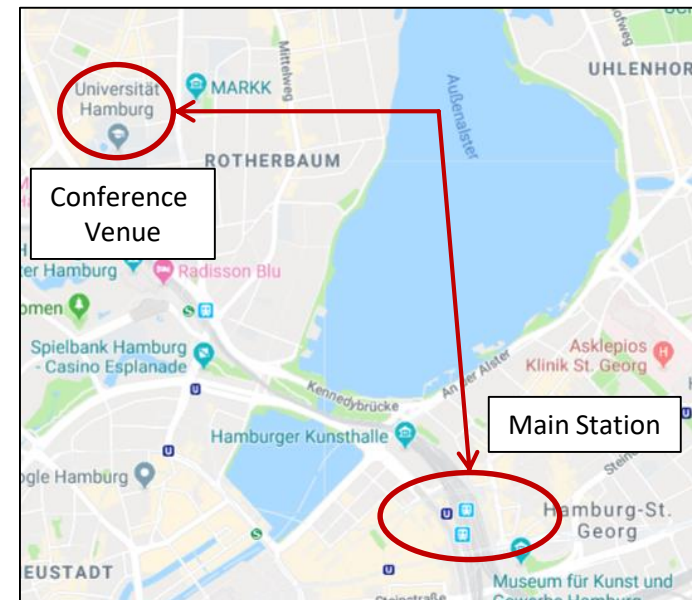
General Emergency Number	112
Firebrigade	112
Police	110
Ambulance	112

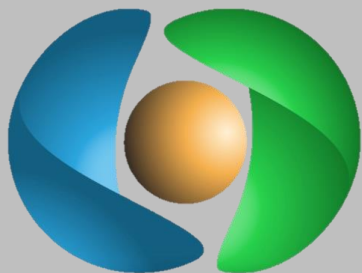
Taxi phone numbers

(+49) 40 211 211
(+49) 40 66 66 66
(+49) 40 211 522

Main Station

Glockengießerwall / Kirchenallee, 20095 Hamburg

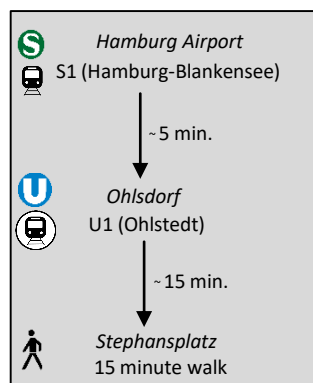
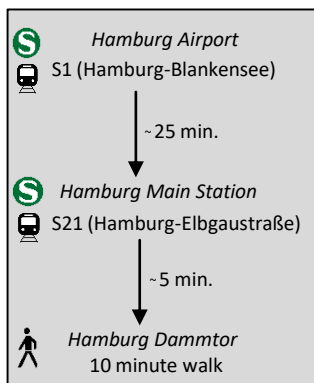




Arrival in Hamburg: Public Transport & Your Way to the Workshop

Transfer from the Airport to the Venue

There are several possibilities to get to the University of Hamburg. Taking public transport to the University takes about 50 minutes (see below for two possible options). Next to public transport, Taxis are available at the airport.



Workshop Venue Address

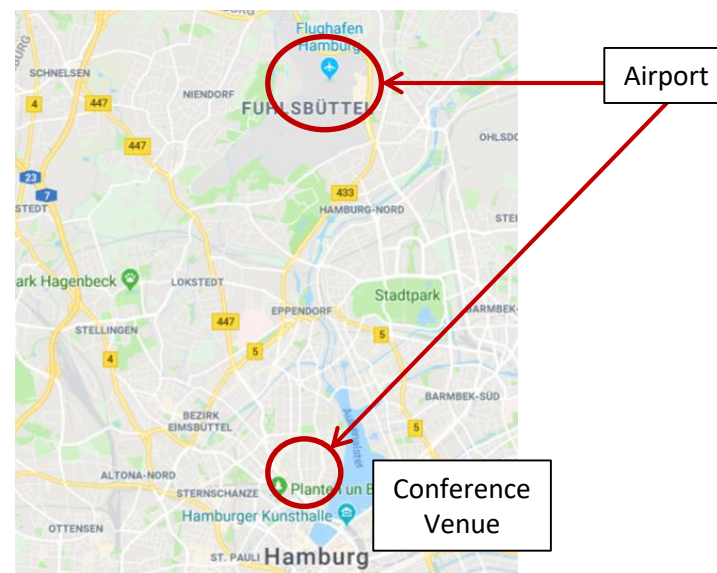
Institute of Technical and Macromolecular Chemistry
University of Hamburg
Bundesstraße 45
20146 Hamburg

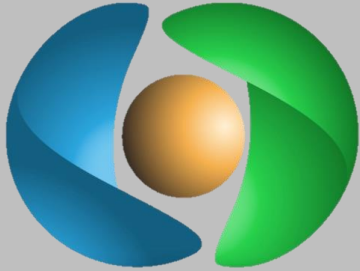
Contact

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

Address: University of Hamburg, Bundesstraße 45, 20146 Hamburg

Dinner on Friday at Hamburger Veermaster

Address: Reeperbahn 162, 20359 Hamburg

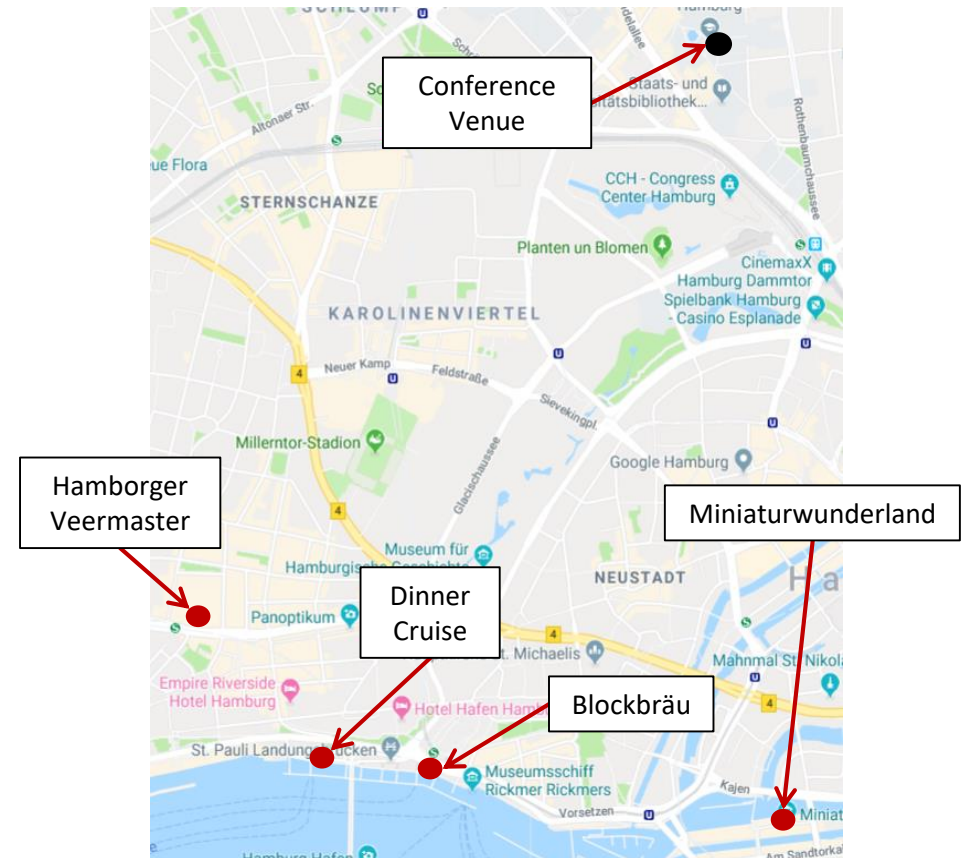
Dinner Cruise on Elbe River on Saturday

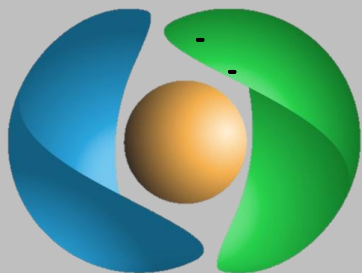
Address: St. Pauli-Landungsbrücken 8-10, 20359 Hamburg

Sunday Lunch at Blockbräu

Address: Bei den St. Pauli-Landungsbrücken 3, 20359 Hamburg

Hamburg City, Overview





Program by Days

Friday, 14th June 2019

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

15:00 -15:15 **Welcome**
Prof. Dr. M. Busch

Session I: Thermodynamics

Chair: Amin Nasresfahani (Queen's University)

15:15 -15:35 **Lenka Krajková** (University of Chemistry and Technology Prague)
Sorption and swelling equilibria relevant for slurry ethylene polymerization

15:35 -15:55 **Maryam T. Agboluaje** (Queen's University)
The effect of polar organic and aqueous solvent on the copolymerization kinetics of an acrylate and functional methacrylate system

15:55 -16:15 **Sebastian M. Dron** (University of San Sebastian)
Improvement of film formation abilities of waterborne latex particles for coating applications.

16:15 -16:35 **Jana Sartorius** (TU Darmstadt)
Kinetic measurements by calorimetry and high-pressure: Decomposition of peroxides depending on solvent and pressure

16:35 -16:55 **Václav Pelc** (University of Chemistry and Technology Prague)
Mathematical Modelling of SAN Copolymerization including Thermal Initiation and Oligomer Formation

16:55 -18:00 **Coffee Break and Poster Session**



18:00 - 18:30 **Dr. Timo Melchin (Wacker)**

19:30 – 21:00 **St. Pauli Night Guard Tour**

21:00 – 23:00 **Dinner at Hamburger Veermaster**

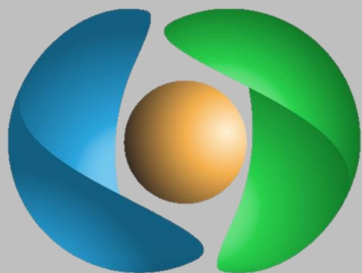


Event kindly sponsored by:



Dinner kindly sponsored by:





Program by Days

Saturday, 15th June 2019

Session II: Modelling

Chair: Fabian Wenzel (University of the Basque Country)

- 09:00 – 09:20 **Paul Peikert** (TU Darmstadt)
Predicting the Branching Structure as well as the Radius of Gyration of LDPE-Homo- and Co-Polymers by Stochastic Modeling
- 09:20 - 09:40 **Christian Zander** (University of Stuttgart)
Propagation of terminal double bonds in the polymerization of N-Vinylpyrrolidone in aqueous solution: modelling strategies and comparison to experimental results
- 09:40 – 10:00 **Felix Kandelhard** (University of Hamburg)
Combined CFD- and Heat-Transfer-Modelling of an Adiabatic Storage Calorimeter
- 10:00 – 10:20 **Francisco Arraez** (University of Ghent)
Model-based study of 2-oxazolines CROP with special attention to side reactions

Coffee Breaks kindly sponsored by:



10:20 - 11:00

Coffee Break and Poster Session



11:00 -11:30

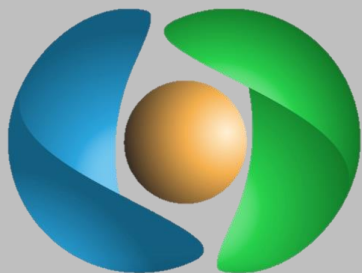
Dr. Stefan Spiegel (Wiley)

Session III: Polyolefines

Chair: Sarah-Elisabeth Dechent (University of Hamburg)

11:30 – 11:50

Sabrine Kardous (University Lyon 1 - LAGEP)
Optimization of grade transition in fluidized-bed reactors accounting for condensed agent effects



Program by Days

Saturday, 15th June 2019

11:50 – 12:10 **Yashmin Blazzio** (University Lyon 1 - LAGEP)
A novel stopped-flow reactor for gas-phase olefin polymerization

12:10 - 12:30 **Jorik Hill** (Martin-Luther-University Halle-Wittenberg)
Kinetic study of the gas phase polymerization of propylene with two Ziegler-Natta catalysts

12:30 -13:00 **Dr. Rolf Bachmann (Covestro)**

13:15 **Lunch: Catering served at conference venue**

Lunch kindly sponsored by:



~~~~~ Session IV: Emulsion Polymerization ~~~~~

Chair: Elisabeth Schulz (TU Darmstadt)

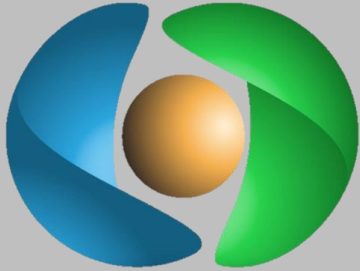
14:30 - 14:50 **Stephanie Schlappa** (University of Potsdam)
In-line monitoring of growth of nano-scaled particles in turbid emulsion polymerization using Photon Density Wave spectroscopy

14:50 – 15:10 **Fabian Wenzel** (University of San Sebastian)
Waterborne Nanoparticles by thiol-ene (Mini)Emulsion Polymerization

15:10 - 15:30 **Laurence Jacob** (University of Hamburg)
In-Line Monitoring of Latex-Particle size distribution during emulsion polymerizations up to 63 wt%

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





Program by Days

Saturday, 15th June 2019

16:30 – 17:00 **Dr. David Eckes (Evonik)**

19:45

Dinner Cruise at Elbe River

Session V: Process Development

Chair: Lenka Krajková (University of Chemistry and Technology Prague)

17:00 – 17:20 **Isabel Kronshorst (TU Darmstadt)**

Implementation of Hydrogen-Injection into a LLDPE-Mini-Plant

17:20 – 17:40 **Amin Nasresfahani (Queens's University)**

Starved Intervals: Optimization of Semi-Batch Solution Radical Copolymerization via Comprehensive Stochastic Modeling and Derivative-Free Algorithms

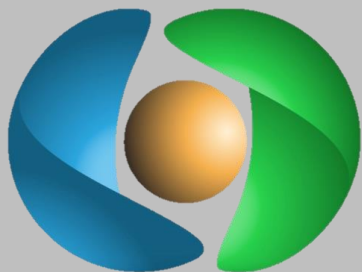
17:40 – 18:00 **Ikenna H. Ezenwajiaku (Queens's University)**

Influence of Ionic Strength from monomer and sodium chloride on aqueous-phase radical copolymerization kinetics of cationic monomers



Dinner Cruise kindly sponsored by:

WACKER



Program by Days

Sunday, 16th June 2019

09:30 **Miniaturwunderland**

Event kindly sponsored by:



12:30 **Sebastian Fries (Novolen)**

13:00 **Poster Prize and Closing Ceremony**

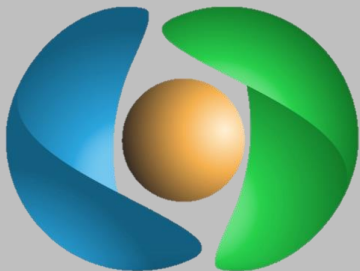
The Prize for the best contribution is kindly sponsored by:

WILEY

12:15 **Lunch at Blockbräu**

Lunch kindly sponsored by:





List of Posters

1. Mathematical Modelling of SAN Copolymerization including Thermal Initiation and Oligomer Formation

Václav Pelc, Juraj Kosek

2. Predicting the Branching Structure as well as the Radius of Gyration of LDPE-Homo- and Co-Polymers by Stochastic Modeling

Paul Peikert, Markus Busch

3. Combined modelling and experimental study of triboelectric charging of polyethylene powders: wall-sheeting and agglomeration

Simon Jantač, Jarmila Kučerová, Ladislav Konopka, Juraj Kosek

4. Experimental and modeling study of ethylene polymerization in gas phase reactors

Amel Ben Mrad, Nida Sheibat-Othman, Timothy F. L. McKenna

5. Sorption and swelling equilibria relevant for slurry ethylene polymerization

Lenka Krajkáková; Barbora Tučková; Juraj Kosek

6. Estimation of Diffusion Coefficients for Multiple Penetrant/Polymer Systems Based on Sorption Data

Rita Ferreira Alves, Timothy F.L. McKenna

7. Combined CFD- and Heat-Transfer-Modelling of an Adiabatic Storage Calorimeter

F. Kandelhard, W. Pauer, H.-U. Moritz

8. Kinetic measurements by calorimetry and high-pressure: Decomposition of peroxides depending on solvent and pressure

J. Sartorius, M. Busch

9. Power compensation calorimetry for studying the kinetics of bulk-phase polymerization of propylene

Sina Valaei, M. Bartke

10. Entanglement Formation mechanism of Ethylene Polymerization by the Heterogeneous Ziegler-Natta Catalysts

Yuming Chena, Wei Lib, Lei Huib, Binbo Jianga, Jingdai Wang, Yongrong Yang

11. Optimization of grade transition in fluidized-bed reactors accounting for condensed agent effects

Sabrina Kardous, Timothy McKenna, Nida Sheibat-Othman

12. Kinetic study of the gas phase polymerization of propylene with two Ziegler-Natta catalysts

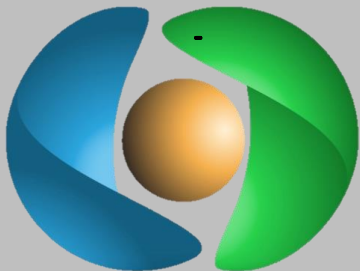
Jorik Hill, Michael Bartke

13. The real-time detection and control of the atmosphere composition: Application in preparation of the PP/EPR in-reactor alloy

Zheng Zheng, Jijiang Hu, Bo-geng Li

14. A novel stopped-flow reactor for gas phase olefin polymerization

Timothy F.L. McKenna, Yashmin Blazzioa, Nida Othmanb, Sebastian Norsica



List of Posters

15. Ring-Opening Polymerization of Epoxides by DMC in Micro-reactor

Jing Zhao, Hong Fan, Bo-geng Li

16. Implementation of Hydrogen-Injection into a LLDPE-Mini-Plant

Isabel M. Kronshorst, Julia Eigenseer, Markus Busch

17. Waterborne Nanoparticles by thiol-ene (Mini)Emulsion Polymerization

F. Wenzel, M. Aquirre, J. R. Leiza

18. In-line monitoring of growth of nano-scaled particles in turbid emulsion polymerization using Photon Density Wave spectroscopy

Stephanie Schlappa, Roland Hass, Oliver Reich, Lena Bressel

19. In-Line Monitoring of Latex-Particle size distribution during emulsion polymerizations up to 63 wt%

Laurence Jacob; Werner Pauer

20. Controlled Synthesis of Polyolefin Copolymers with Rapid Curability for Photovoltaic Cell Encapsulation

Liqiong Luo, Kailun Zhang, Pingwei Liu, Bo-Geng Li, Wen-Jun Wang, Guangda Zhou

21. Influence of Particle Morphology on Film Drying Stresses

Hesham Abdeldaim, José M. Asua

22. Fully bio-derivable CO₂ fixating polymers for HNIPU applications

S.-E. Dechent, A. W. Kleij, G. A Luinstra

23. High Barrier Waterborne Polysulfide Dispersions

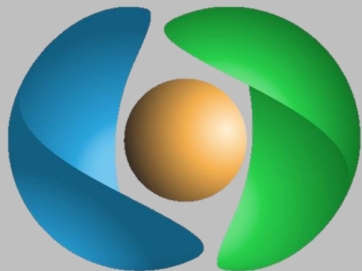
J. Elgoyhen, R. Tomovska.

24. Determination of micromixing efficiency in viscous media

E. Arian, W. Pauer

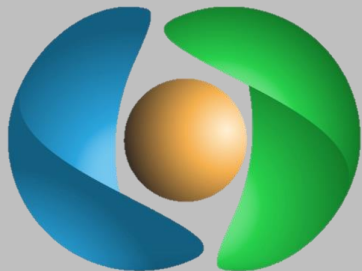
25. Refractive Index Increments of EVA-Copolymers

Elisabeth Schulz, Markus Busch



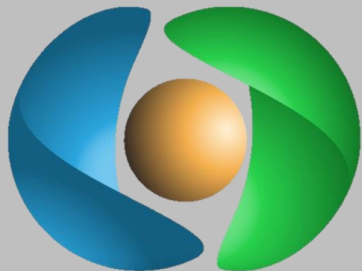
List of Participants

	First name	Surname	Institution
1	Hesham	Abdeldaim	University of the Basque Country
2	Maryam	Agboluaje	Queen's University
3	Elias	Arian	University of Hamburg
4	Francisco	Arraez	University of Ghent
5	Rolf	Bachmann	Covestro
6	Amel	Ben Mrad	University of Lyon
7	Yashmin	Blazzio	University of Lyon
8	Markus	Busch	TU Darmstadt
9	Yuming	Chen	Zhejiang University
10	Sarah-Elisabeth	Dechent	University of Hamburg
11	Sebastian	Dron	University of the Basque Country
12	David	Eckes	Evonik Technology & Infrastructure GmbH
13	Justine	Elgoyhen	University of the Basque Country



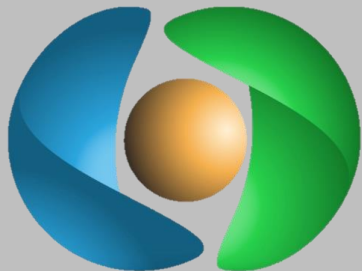
List of Participants

	First Name	Surname	Institution
14	Sebastian	Eller	University of Hamburg
15	Ikenna Henry	Ezenwajiaku	Queen's University
16	Rita	Ferreira Alves	University of Lyon
17	Sebastian	Fries	Lummus Novolen Technology GmbH
18	Nina	Heidarzadeh	Queen's University
19	Jorik	Hill	Martin-Luther-University of Halle-Wittenberg
20	Laurence	Jacob	University of Hamburg
21	Simon	Jantač	University of Chemistry and Technology Prague
22	Felix	Kandelhard	University of Hamburg
23	Sabrine	Kardous	University of Claude Bernard
24	Lenka	Krajáková	University of Chemistry and Technology Prague
25	Thomas	Kroener	BASF
26	Isabel	Kronshorst	TU Darmstadt



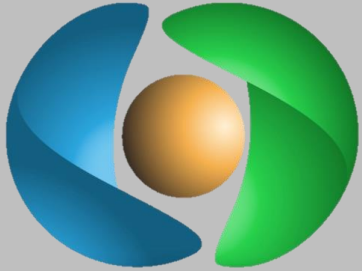
List of Participants

	First Name	Surname	Institution
27	Li Qiong	Luo	Zhejiang University
28	Sara	Marcos Ortega	Sabic
29	Timo	Melchin	Wacker
30	Amin	Nasresfahani	Queen's University
31	Mariana	Nogueira Duarte	BASF
32	Nida	Othman	University of Lyon
33	Werner	Pauer	University of Hamburg
34	Paul	Peikert	TU Darmstadt
35	Václav	Pelc	University of Chemistry and Technology Prague
36	Kristina	Pflug	University of Hamburg
37	Jana	Sartorius	TU Darmstadt
38	Stephanie	Schlappa	University of Potsdam
39	Elisabeth	Schulz	TU Darmstadt



List of Participants

	First Name	Surname	Institution
40	Stefan	Spiegel	Wiley
41	Sarah-Franziska	Stahl	University of Hamburg
42	Sheraz	Tariq	University of the Basque Country
43	Ursula	Tracht	Arlanxeo
44	Sina	Valaei	Martin-Luther-University of Halle-Wittenberg
45	Fabian	Wenzel	University of the Basque Country
46	Christian	Zander	University of Stuttgart
47	Jing	Zhao	Zhejiang University
48	Zheng	Zheng	Zhejiang University
49	Alexandr	Zubov	University of Chemistry and Technology Prague
50			
51			
52			



Book of Abstracts

1. Lenka Krajáková
2. Maryam Agboluaje
3. Sebastian Dron
4. Jana Sartorius
5. Václav Pelc
6. Paul Peikert
7. Christian Zander
8. Felix Kandelhard
9. Francisco Arraez
10. Sabrine Kardous
11. Yashmin Blazzio
12. Jorik Hill
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18. Ikenna Ezenwajiaku
19. Simon Jantač
20. Amel Ben Mrad
21. Rita Ferreira Alves
22. Sina Valaei
23. Yuming Chen
24. Zheng Zheng
25. Jing Zhao
26. Liqiong Luo
27. Hesham Abdeldaim
28. Sarah-Elisabeth Dechent
29. Justine Elgoyhen
30. Elias Arian
31. Elisabeth Schulz

Improvement of film formation abilities of waterborne latex particles for coating applications

Sebastian M. Dron, M. Paulis

Polymat, University of the Basque Country San Sebastian, Spain

Waterborne latex dispersions accessible through emulsion polymerisation play an important role in the application field of coatings, especially for paints. However, even with benefits like the reduced volatile organic compounds (VOC) level, compared with solvent borne coating systems, only 16% of industrial paints are waterborne latex coatings. This could be owed to some technical challenges, which occur to reach properties such as hardness, block and print resistance. However, considering new environmental regulations the dramatic decrease of VOCs in coating products will be one of the most important goals during the development of new applications in this area. Even in waterborne emulsion polymers, the use of a certain amount of VOCs is necessary to obtain films with good properties (coming from a relative high glass transition temperature (T_g) polymer) at ambient temperature (with low minimum film formation temperature (MFFT)). Instead of VOCs temporary plasticizers can be used. In this project, Temporary Hydro Plasticizers (THPs) and Temporary Oligomer Plasticizers (TOP) are investigated to lower the MFFT without influencing the T_g . THPs use water to obtain the plasticizing effect, whereas TOPs use short chains, consisting out of the same monomers as the latex. As basic polymer a BA/MMA (40/60) latex with 50% solids content ($T_g = 30^\circ\text{C}$, MFFT = 25°C) was used. As THP amongst others, polyethylene glycol methacrylate (PEGMA) and itaconic acid (ITA) were used. With these THPs the MFFT could be decreased down to $14 \pm 2^\circ\text{C}$, obtaining films with suitable mechanical and water resistance properties. A DSC measurement method was developed to study how much water causes the plasticization effect and its behaviour in the polymer matrix. For the TOPs, the oligomers were synthesized in situ during the emulsion polymerization using a chain transfer agent (CTA). The TOPs decreased the MFFT down to $17 \pm 1^\circ\text{C}$. The combination of both approaches allowed synthesizing a latex with a MFFT of $5 \pm 1^\circ\text{C}$ and a T_g of 31°C which reach his optimal mechanical performance independent from the temperature. Currently the produced latices are used, in cooperation with the industry, as binders for paint formulation to investigate their application performance.

Your notes:

Kinetic measurements by calorimetry and high-pressure: Decomposition of peroxides depending on solvent and pressure

J. Sartorius, M. Busch

TU Darmstadt, Ernst-Berl-Institut für Technische und Makromolekulare Chemie, Alarich-Weiss-Straße 8, 64287 Darmstadt, Germany; e-mail: markus.busch@pre.tu-darmstadt.de

Radical polymerization is widely applied in industrial production using peroxides as initiators. To guarantee a smooth start-up of polymerization a mixture of peroxides is used. Therefore, peroxides with complementary temperatures of decomposition are combined to stabilize the number of radicals during temperature changes. To calculate suitable peroxide concentration, kinetic parameters such as reaction rate and activation energy has to be known at reaction conditions in temperature and pressure dependence. Data sets are often not available or do not include the influence of solubility or pressure.

Polymers like LDPE are industrially synthesized under high pressure up to 3000 bar and temperature around 300°C. At these conditions, some classical techniques of kinetic measurement are difficult to perform, but high-pressure calorimetry can be carried out using massive and specialized devices. Calorimetry is sensitive to reaction progress and slight changes between different conditions because decomposition of peroxides is highly exothermic. This can be carried out in high-pressure crucibles in a DSC device withstanding pressure up to 800 bar or in a Transitiometer withstanding pressure up to 2000 bar. Great advantage of calorimetric measurements in a Transitiometer is the feasibility of extreme conditions and the simultaneous control of pressure, temperature and volume. Thus, the pressure is kept constant to prevent critical pressure build up and enables to determine pressure dependency.^[1]

Kinetics of radical polymerization to LDPE are a highly complex reaction network, so that data needs to be measured partwise of single reactions getting reliable results. First step of the reaction network is the decomposition of peroxides creating radicals. Therefore, the decomposition of peroxides is measured without monomer surrounding. This way the overlap of decomposition reaction with propagation, termination or transfer is prevented.

The peroxide solution is heated up in tightly closed and pressurized crucibles with a certain heating rate while the calorimetric signal is measured. The scan starts below the onset-temperature and cover the complete decomposition creating an exothermal peak. Analysing this, the temperature of decomposition, the enthalpy, activation energy and pre-exponential factor is obtained. The enthalpy is the integral of the time-dependent calorimetric signal. Through Kissinger-method or Borchardt-Daniels-method as a n^{th} order-method, the activation energy and the pre-exponential factor is calculated.

For the Kissinger-method, measurements with varying heating rates are necessary and an order of reaction of $n=1$ is assumed. With the Borchardt-Daniels-method, the reaction order is an additional variable and activation energy and pre-exponential factor are calculated through a multilinear fit out of a single measurement. Using wide ranges of heating rates for the Kissinger-method the reliability is increased and the assumed order of reaction $n=1$ can be verified with the n^{th} order-method. Combining kinetic and enthalpy data, the heat input by a reaction is known.

Present results of DSC scans show a correlation of decomposition temperature with the polarity and heat capacity of the solvent. Besides solvent effects, kinetic parameters show a dependency on pressure. Solvent properties also influence the enthalpy of decomposition. The enthalpy increases with increasing polarity of the solvent and decreases with increasing pressure. Combining results of DSC and Transitiometer, wide ranges of heating rates and pressure can be monitored and results of both devices can be compared.

Under high-pressure conditions of radical polymerization, peroxides are surrounded by a high viscose matrix of a polymer-monomer mixture. Replacing solvent by polymer melt or waxes for measurements could be a step forward to more practical reaction conditions.

[1] S. L. Randzio, J.-P. E. Grolier, J. R. Quint, D. J. Eatough, E. A. Lewis, and L. D. Hansen, *Int. J. Thermophys* **1994**, 15(3): p.415-440.

Your notes:

Propagation of terminal double bonds in the polymerization of N-Vinylpyrrolidone in aqueous solution: modelling strategies and comparison to experimental results

*C. Zander*¹, *K.-D. Hungenberg*², *T. Schall*¹, *C. Schwede*³, *U. Nieken*¹

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Specialty polymers, e.g. Polyvinylpyrrolidone, are mostly produced in batch or semi-batch processes due to the need for flexibility in the production of this product class. In the course of process intensification, new processes in smart-scale reactor systems which can be operated continuously are under investigation to improve process control and energy efficiency. One of the major problems in the development of processes in such reactor systems is the occurrence of fouling deposits which prohibit the continuous operation. The latter may be formed by side reactions leading to branched or crosslinked polymer chains which form an insoluble polymer gel. To predict process windows in which reactors can be operated without the formation of fouling deposits, kinetic models which predict polymer properties quantitatively are essential. Since these models are to be used in extensive parameter variations or CFD simulations, the computational effort should be as small as possible while the relevant structural property information must be captured as accurately as necessary.

The propagation and termination kinetics of the system of interest are well known and published in literature [1,2]. While it is clear that side reactions are relevant in the reaction mechanism [3], their nature and especially their rates are still in the focus of research. Recent results suggest that production of and propagation of terminal double bonds are important parts of the branching mechanism [4]. The work presented in this contribution is based on these findings. Starting from a multi-dimensional property distribution, different reduced models have been derived using so-called pseudo-distributions [5,6] and validated. Further reduction of model complexity has been achieved by transferring information from more detailed models into simplified models which are suitable for fast calculations.

Different models with different levels of complexity and detail of information will be introduced and compared. The simplified models have been used for parameter estimations and will finally be compared to CSTR experiments. The model predictions and experimentally observed values are in very good agreement.

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Your notes:

Optimization of grade transition in fluidized-bed reactors accounting for condensed agent effects

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Polyethylene (PE) is the most widely produced polymer in the world. The variety of PE applications requires different grade specifications to suit the market demand. Most processes used to make linear low density polyethylene (LLDPE) are gas phase processes to avoid problems linked to the solubility of amorphous polymers in liquid hydrocarbons. These processes are clean, solvent-free and less energy consuming than free radical processes (lower temperature and pressure), but their productivity is limited by the heat generated by the reaction. Fluidized-bed reactors (FBRs) are the only reactors that can be used, from an economic point of view, to make many grades of LLDPE or HDPE by changing the operating conditions (e.g. Pressure, Temperature...).^[1]

In order to overcome the issue of heat transfer in gas processes, “condensed mode cooling” is frequently employed, where induced condensing agents (ICAs), such as isobutane, are injected in either liquid or vapor form in order to absorb part of the reaction heat.^[2] However, it was observed that the presence of ICA influences the absorption of monomer into the polymer and consequently the reaction rate and the polymer properties (e.g. the polymer molecular weight and density).

In this work, a combined kinetic and thermodynamic model (based on Sanchez-Lacombe equation of state) is developed for the catalytic copolymerization of ethylene with 1-butene in an FBR. This model is able to predict the co-solubility effect of the ICA (isobutene) and thus its effect on the reaction rate and the polymer properties. However, the Sanchez-Lacombe model is not available for a quaternary system (here PE, ethylene, ICA and co-monomer) and no thermodynamic data is available in the literature for this system. Therefore, the co-solubility effect of ICA (isobutane) on ethylene was evaluated in a ternary system (PE, ethylene and ICA) and was assumed to remain unchained when adding the co-monomer (i.e. assuming no interaction between ICA and the co-monomer). Moreover, the solubility data of the co-monomer (1-butene) in the polymer is available only in a binary system, so it was approximated to obey the same trend as the ICA in a ternary system (as they have similar free volumes and thermodynamic properties). These two assumptions allow us to estimate the concentrations of ethylene and co-monomer in the amorphous polymer, and therefore to calculate the copolymerization rate and the copolymer properties.

This model was then used to optimize the transition between different grades of LLDPE using a dynamic optimization procedure, which provides the optimal flow rate profiles of hydrogen and co-monomer. The objective function allows for minimization of the quantity of off-spec during grade transitions, where the primary controlled variables are the melt index (MI), which is related to the polymer molecular weight (that is determined by transfer to hydrogen and the co-monomer fraction in the copolymer), and the polymer density (ρ) which is controlled by the co-monomer fraction in the copolymer. This strategy demonstrates the importance of accounting for the effect of the induced condensing agent within grade transition optimization, as it has a direct effect on the polymer properties and the reaction rate.

The proposed model is expected to be a powerful tool for fundamental understanding of gas-phase polyolefin polymerization, and can be used for improving PE product quality in the polymer industry, with minimized waste and energy consumption during the transition while maintaining the process safety.

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Your notes:

Kinetic study of the gas phase polymerization of propylene with two Ziegler-Natta catalysts

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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.

During the coordinative polymerization of propylene, the polymer chains grow at the active sites of the catalyst. The active center determines the rate of monomer incorporation and thus the polymerization kinetics are catalyst dependent. The ongoing industrial catalyst development requires kinetic evaluation of newly designed catalysts. One important aspect is the lab-scale kinetic investigation of these catalysts under industrial relevant conditions. The gathered results are essential for the next scale-up step. Combining the experimental output with modeling and simulation enhances process development. For instance, lab-scale kinetics can be combined with pilot-scale process dynamics to precisely plan pilot-scale tests.

The current contribution deals with the kinetic investigation of two commercial Ziegler-Natta catalysts. Polymerization experiments were conducted 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. The effects of hydrogen and a prepolymerization step were studied. Based on the experimental results, a kinetic model was developed. The model could adequately describe the experimental findings within the measurement errors.

Your notes:

In-line monitoring of growth of nano-scaled particles in turbid emulsion polymerization using Photon Density Wave spectroscopy

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Highly concentrated liquid dispersions with particles and droplets in the nanometer and micrometer scale are of wide technical importance. Examples are found in polymer and coatings industry, in food industry and in biotechnology. Such emulsions or suspensions often exhibit strong light scattering, thus limiting conventional optical process analytical technologies in their application range e.g. for particle sizing or concentration determination.

A contamination- and calibration-free process analytical technology suitable for highest concentrations (i.e. > 40 vol%), stirred or flowing systems and for potentially explosive environments is found in in-line or on-line Photon Density Wave (PDW) spectroscopy [1-2]. It allows for the independent quantification of the absorption and scattering properties of disperse materials, i.e. the absorption and reduced scattering coefficients, respectively. The absorption coefficient exhibits information about the chemical composition and/or the temperature of the material. The reduced scattering coefficient however is related to the size of the dispersed particles. Sizes are determined applying Mie theory for spherical particles and theory of dependent light scattering [3].

As a chemical model process the radical emulsion polymerization of vinyl esters stabilized by vinylalcohols (protective colloid) was investigated by PDW spectroscopy. Vinylesters were polymerized to have specifically set particle sizes and particle size distributions by changing the type of redox initiator, amount of initial protective colloid and addition rates of educts.

With a time resolution in the minute scale the growth of formed nanoparticles could be monitored during emulsion polymerization by PDW spectroscopy. Highly turbid polyvinylester dispersions with mean particle sizes in the nanometer or lower micrometer range and with solid contents of approx. 50% were achieved. Particle size distributions obtained without dilution in the final product by PDW spectroscopy were in good agreement with conventional off-line and dilution based analysis techniques as Scanning Electron Microscopy, Static Light Scattering and Dynamic Light Scattering.

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Your notes:

Waterborne Nanoparticles by thiol-ene (Mini)Emulsion Polymerization

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POLYMAT and Kimika Aplikatua Saila, Kimika Fakultatea, University of the Basque Country UPV/EHU, Joxe Mari Korta Zentroa, Tolosa Hiribidea 72, 20018 Donostia-San Sebastián, Spain

Thiol-ene polymerization takes place between a thiol functional group and a ene functional group. Despite being a radical polymerization, it follows step-growth mechanism. Therefore, generally stoichiometric amounts of the monomers are used. Thiol-ene polymerization exhibits many advantages, such as the extremely rapid reactions due to the insensitiveness of the reactants to oxygen and moisture, which are near to quantum yields. Thiol-ene polymerizations show properties of so called “click” reaction. Furthermore, a broad range of thiols and enes can be used. Due to this versatility and robustness thiol-ene polymerization is feasible for a wide range of applications such as protective coatings, optical and biomedical devices, coupling and bioorganic modifications.^[1]

On the other hand, waterborne polymerizations are gaining more and more attention over solvent borne systems due to increasing restrictions regarding volatile organic compounds (VOC). However, because of the rather hydrophobic nature of the dienes it is challenging to introduce thiol-ene polymerization into a conventional emulsion polymerization process, whereas the possibility to do so by using a less hydrophobic diene was reported by D. Shipp et al.^[2], in most cases a miniemulsion polymerization process is necessary.

The aim within this project is to investigate the suitability of thiol-ene polymerization for the production of waterborne pressure sensitive adhesives (PSAs). PSAs are viscoelastic materials that can adhere strongly to solid surfaces upon application of a light contact pressure and in short contact times.^[3] Mobility of the polymers chains is needed for the PSA to be able to adhere to the substrate and to provide tack. But also a certain degree of stability to provide cohesion and resistance against creep is needed. Polymers coming from thiol-ene polymerization exhibit very low T_g s because of their linear nature. Therefore, different kinds of thiol and ene monomers were investigated in this work, either in emulsion or miniemulsion polymerization, to tune the T_g of the polymer. Furthermore, monomers with a functionality higher than two were used to introduce crosslinking in order to provide increased cohesiveness to the waterborne PSA.

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Your notes:

In-Line Monitoring of Latex-Particle size distribution during emulsion polymerizations up to 63 wt%

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The most common methods for the determination of mean particle size and particle size distribution mainly perform offline analysis in diluted solutions, which poses numerous disadvantages. Therefore, an inline measurement method would be preferable. Thus, the relatively new method of photon density wave (PDW) spectroscopy ^[1] was investigated for its suitability for inline particle size measurement in high solid content emulsion polymerization.

For this reason, emulsion copolymerization of vinyl acetate and Versa® 10 in a molar ratio of 9:1, and with varying emulsifier content, were carried out with different target particle sizes, both in batch and semi-batch, achieving a size range of 50 to 325 nm. For the initiation of the copolymerization, a redox initiator system, consisting of L-ascorbic acid, tert-butyl hydroperoxide and ammonium iron (III) sulfate, was used. The results of PDW spectroscopy were compared with those of conventional offline measurement methods, such as dynamic light scattering (DLS) and sedimentation analysis, by means of a disc centrifuge.

In order to attest the suitability of the PDW method, the measured particle diameters were plotted against each other. A linear fit of the results comparing PDW spectroscopy with a disc centrifuge gave a slope of (0.94 ± 0.06) and a y-intercept value of (7 ± 12) nm. The fit has a correlation quality of 98% and a corrected R^2 of 95%. This corresponds to a very good agreement of the data. The linear fit of the comparison between PDW spectroscopy and DLS gave a slope of (0.99 ± 0.14) and a y-intercept value of (-47 ± 24) nm. The correlation quality of the fit is 92% and the corrected R^2 is 84%. The suitability of PDW-spectroscopy was proven experimentally with a polymer content of up to 63 wt%.

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Your notes:

Implementation of Hydrogen-Injection into a LLDPE-Mini-Plant

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As plastics play a fundamental role in modern society, controlling its properties is of major importance. Linear low-density polyethylene (LLDPE) is a co-polymer of ethylene and an α -olefin. It is prepared in a catalytic solution polymerization and offers a variety of properties depending on molecular weight, used co-monomer and amount of implemented co-monomer. During the polymerization process, changing one of these parameters influences the others. As the aspects interfere with each other mutually, a reduction of the system's complexity is necessary in order to regulate a parameter separately. The important aspects that influence the properties of LLDPE are the amount of co-monomer, the type of co-monomer, the conversion and the degree of polymerization. In order to compare different side chain lengths different co-monomers must be accessible. Therefore, an existing LLDPE solution mini-plant which has a pre-existing liquid monomer dosing is expanded by a liquefied gas dosing.

For the analysis of the impact of the short-chain branching length on the polymer properties, the molecular weights of the polymers have to be similar. Therefore, a chain transfer dosing is introduced using hydrogen. By this the degree of polymerization can be adjusted to a certain value. By oppressing the influence of degree of polymerization on polymer properties, the influence of the side chain lengths can be estimated separately.

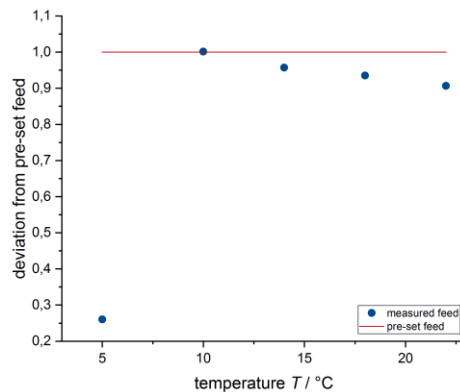


Figure 1: Deviation of feed rate from the pre-set feed rate as a measure of temperature.

The implementation of both adjustments is separately validated on the correct operation. Figure 1 shows the validation of the transport of the liquefied gas. It depicts the ratio between the actual feed rate and the pre-set feed rate as a measure of the pump head's temperature. The deviation which is caused by cavitation can be reduced and a proper transport of the liquefied gas is validated.

Additional to the verification of a correct operation, for the hydrogen dosage a proper method of feeding has to be chosen. The impact of hydrogen concentration transients is shown in figure 2. As part of this work a method of feeding hydrogen to the system without transients was developed.

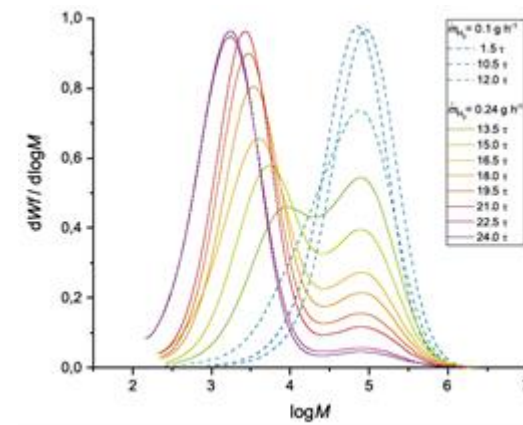


Figure 2: Effect of the increasing hydrogen concentration in the reactor on the molecular weight distribution.

With both of these adjustments, the mini-plant can now be used to prepare a variety of copolymers differing in amount and length of side branching at controlled molecular weights.

Acknowledgement: Borealis AG

Your notes:

Starved Intervals: Optimization of Semi-Batch Solution Radical Copolymerization via Comprehensive Stochastic Modeling and Derivative-Free Algorithms

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Theoretical models are vital in bridging kinetic and process procedures to the resulting structures and to tackle the design complexities in synthesizing engineered materials. Discretizing the polymerization time into multiple constant starved-feed intervals allows kinetic Monte Carlo simulations to be utilized in semi-batch recipe optimizations where manipulating the independent feed streams are regarded as a gateway of improving the process. This concept is coupled with an accelerated stochastic model [1] developed for semi-batch solution free radical copolymerization of acrylate/methacrylates synthesized at high-temperatures; Considering secondary reactions such as backbiting, macromonomer production/consumption, and midchain radicals provides a realistic off-line optimization. It uses the reaction time intervals to regulate flowrates of the feed streams. Derivative-free optimization algorithms (e.g., *Pattern Search*[2] and *Particle Swarm*[3]) are utilized to effectively derive the polymer product properties to the target value. The developed concept of starved-intervals is found to be a promising strategy compared to the traditional starved-semi-batch recipes often used for obtaining low-molecular-mass high-value polymer resins, reducing the total polymerization time by 75% while simultaneously improving the quality of the product and the productivity of the process.

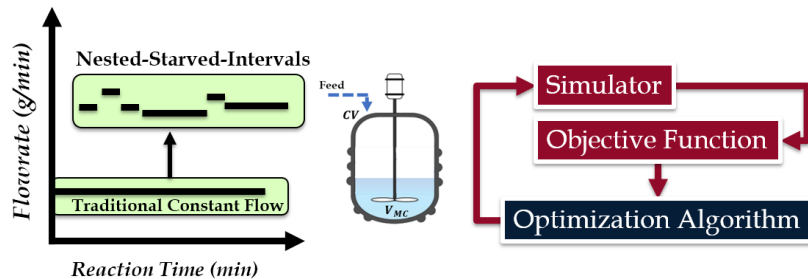


Figure 1: A Graphical abstract depicting the concept of the technique compared to the traditional starved-feed operation.

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Your notes:

INFLUENCE OF IONIC STRENGTH FROM MONOMER AND SODIUM CHLORIDE ON AQUEOUS-PHASE RADICAL COPOLYMERIZATION KINETICS OF CATIONIC MONOMERS

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Aqueous-phase radical polymerization kinetics of industrially relevant water-soluble polymers have been critically investigated using the in-situ NMR technique. This specialized experimental technique has greatly improved the understanding of these systems and allows for reliable data collection at monomer concentrations up to 40 wt%, following both overall monomer conversions as well as composition drift in a copolymerization system.

Our work focuses on the effects of varying ionic strength contributions from monomer contents and sodium chloride (NaCl) on kinetics of [2-(methacryloyloxy)ethyl]trimethylammonium chloride (TMAEMC) and 3-(methacryloylamino)propyl]trimethylammonium chloride (MAPTAC), cationic monomers containing an ester and amide functional groups, respectively, copolymerized with both non-ionized (AA) and fully-ionized (NaA) acrylic acid to form copolymers with applications as cationic flocculating agents in water treatment. The drift in monomer composition was found to be enhanced with increasing ionic strength of monomer and NaCl. However, as molar fractions of TMAEMC and MAPTAC decrease in solution, this effect diminished with more pronounced effects in copolymerization with NaA (as shown in Fig. 1 for AA-TMAEMC). This could be attributed to NaA cross propagation being more favoured than AA due to electrostatic interactions while homopropagation of TMAEMC remains relatively unchanged.

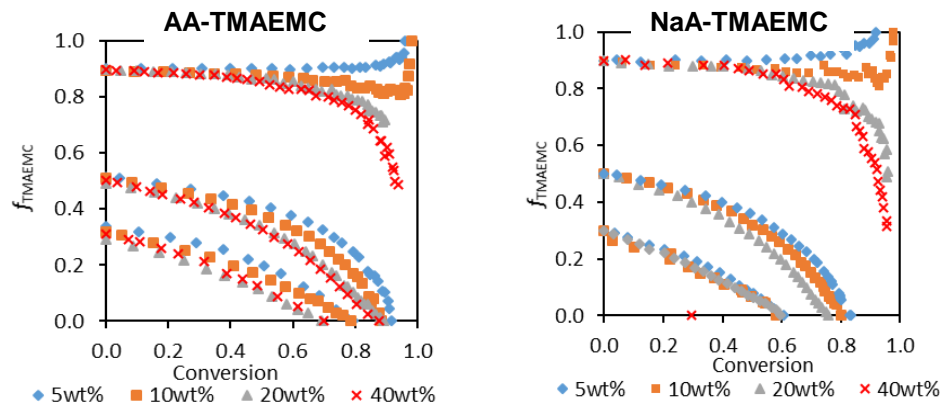


Figure 1: Comonomer composition drifts at varied monomer contents in batch copolymerizations of TMAEMC with non-ionized AA (left) and fully ionized AA (right) at 50°C and 0.4 wt. % V-50, and different initial monomer compositions.

A model to capture the composition drifts of AA/NaA-TMAEMC copolymerization has been successfully completed which accurately predicts the effects of ionic strength from monomer contents and NaCl as well.

Your notes:

EXPERIMENTAL AND MODELING STUDY OF ETHYLENE POLYMERIZATION IN GAS PHASE REACTORS

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A widely-used approach to control overheating in the gas phase polyethylene systems is the so-called "condensed operating mode" where liquid species are injected together with the monomer feed [1]. These liquid species, usually alkanes, are called "induced condensing agents" (ICA). Upon entering the reactor, the liquefied components vaporize and the latent heat of evaporation helps to cool the system. 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]. Different thermodynamic models are available that can capture this type of behavior, but all of them rely on a set of adjustable parameters than cannot be predicted a priori. To add to the complications, very limited solubility data is available for multicomponent systems; it is therefore very difficult to obtain realistic model parameters for olefin polymerization systems.

We have chosen to work with the Sanchez-Lacombe equation of state, as it is one of the most widely applied thermodynamic models in polymer industry [3]. The interaction parameters used in the Sanchez-Lacombe EoS will be identified by fitting equilibrium solubility data which are measured experimentally using a pressure-decay technique in standard laboratory equipment. Experiments are carried out in a 2 liter stirred reactor, operated under a range of pressures from atmospheric to 30 bars, and over a range of temperatures. A simple operating protocol allows us to generate solubility data for a limited cost. After introducing a known quantity of polymer into the reactor, an insoluble gas (e.g. Argon) is used to carefully measure the volume of the void space among the polymer particles and in the feed lines. Then, mixtures of soluble gases are injected into the reactor, the pressure is measured and since we know the volume of the gas phase, we know the number of moles of gas in the void. The difference between the moles fed to the reactor and the moles in the gas phase gives us the solubility. Gas phase composition is measured with an upgraded Micro GC, allowing us to estimate individual solubilities in mixes of different process gases.

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Your notes:

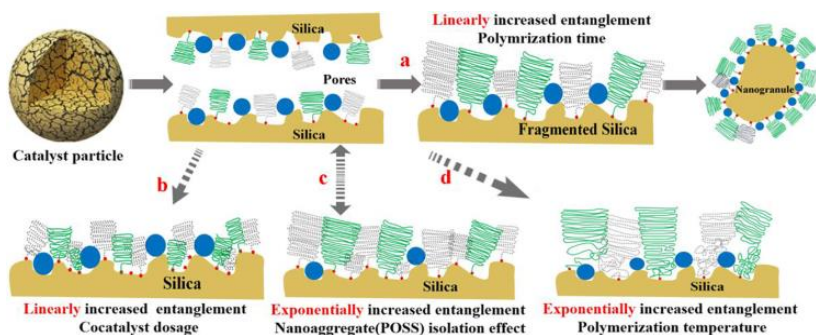
Entanglement Formation mechanism of Ethylene Polymerization by the Heterogeneous Ziegler-Natta Catalysts

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Chain entanglement was very important for adjusting the processability and mechanical property of nascent ultrahigh molecular weight polyethylene (UHMWPE). So far, it is still a mystery to unravel the formation mechanism of entanglements when the ethylene polymerization is conducted by the supported heterogeneous catalysts. In this study, a series of weakly entangled UHMWPE was synthesized by the polyhedral oligomeric silsesquioxane/MgCl₂ nanoaggregates modified Ziegler-Natta catalysts. The structure of nanoaggregates was evaluated by X-ray photoelectron spectroscopy (XPS), Density functional theory (DFT) simulations, and Scanning probe microscope (SPM) experiments, where the coordination strategy of MgCl₂ and hydroxyl of POSS was investigated. These nanoaggregates presented extremely low activity on ethylene polymerization and were proved to serve as isolators for separating the active sites and growing chains, where the entanglement density of nascent UHMWPE was non-linearly decayed with the increased numbers of nanoaggregates. Importantly, this non-linearly decayed effect contributed by increasing numbers of POSS/MgCl₂ isolators offset the exponential increment of entanglements upon rising the temperature, which was the essential reason for the successful synthesis of weakly entangled UHMWPE even at 85 °C. Finally, we have proposed the dependence and sensitivity of $G_{N^*}(t=0)$ (*i.e.*, indicating the initial entanglement density of nascent polymers) on the polymerization activity, which was able to quantitatively trace the formation of entanglements during polymerization through the heterogeneous catalyst.



Scheme 1. The entanglement formation mechanism diagram of nascent polyethylene with different polymerization conditions.

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Your notes:

Ring-Opening Polymerization of Epoxides by DMC in Micro-reactor

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Polyols obtained by ring-opening polymerization of epoxides catalyzed by Co-Zn double metal cyanides (Co-Zn DMC) have many advantages such as narrow molecular weight distribution, lower unsaturated degree and less in impurities, which benefits the subsequent polyurethane foaming process. However, the reaction system is quite dangerous in tank reactor because it is highly exothermic, so it has to be conducted in way of semi-continuous feed-starving of monomer in industry. This severely influences the production efficiency and still needs huge investments in equipments. Micro-reactor improves the operation safety for the highly exothermic reaction due to its small volume, large surface to volume ratio. Herein, we report the ring-opening polymerization of propylene oxide catalyzed by Co-Zn DMC in micro-reactor system, propylene oxide and prepolymer of polypropylene glycol (PPG) containing Co-Zn DMC catalyst were pumped into the preheat lines, mixed in the micromixer and flowed through the delayed lines to the outlet where a back pressure valve was connected, and as a result, polyols of different molecular weight were obtained within several minutes and their molecular weight distribution (characterized by polydispersity index, abbreviated as PDI) was usually quite narrow ($PDI < 1.1$). In addition, we studied the effects of residence time, temperature, catalyst concentration, reactants ratio and pressure on conversion, molecular weight and molecular weight distribution. These results show that the micro-reactor has good application prospects in industry of polyols.

Your notes:

Controlled Synthesis of Polyolefin Copolymers with Rapid Curability for Photovoltaic Cell Encapsulation

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Polymers such as ethylene–vinyl acetate (EVA) copolymers have been widely used as encapsulants in photovoltaic cell modules to prolong their outdoor lifetime. However, EVAs are prone to yellowing after long-term usage, which significantly reduces the photoelectric conversion efficiency of the cells. Alternatively, polyolefins (POs) with outstanding outdoor stability have been considered as a highly promising encapsulant material for the photovoltaic cell encapsulation. The inertness of the POs, however, results in a slow curing during the cell encapsulation process.

In this study, we address the problem through a polymer product engineering approach by controllably introducing pedant vinyl groups into ethylene-octene copolymers via terpolymerization of ethylene, octane-1, and an asymmetric diene. The vinyl functionalities are ready to react with crosslinking agents, which distinctly increases the PO curing rate measured by storage modulus (G'). We are able to precisely tune the vinyl content in the POs from 0 to 4.01 mol% through engineering the polymerization processes. Moreover, under the same crosslinking reaction condition, G' was significantly increased from 11294 pa to 57090 pa. Interestingly, we also observed that the crosslinking reaction was beneficial to the product transparency and volume resistivity, and did not affect the damp-heat and UV aging performances of the resulting PO films.

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[2] Liqiong Luo, Kailun Zhang, Pingwei Liu, Guangda Zhou, Bo-Geng Li, and Wen-Jun Wang. in preparation.

Your notes:

Influence of Particle Morphology on Film Drying Stresses

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Adverse impacts on health and the environment are forcing paint and coating manufacturers to replace the volatile organic compounds in traditional formulations with water-based formulations. One of the approaches to achieve high film forming ability with excellent mechanical properties from aqueous dispersions is the use of heterogenous particles with two phases. One phase with low Tg for coalescence forming the layer and the other phase with high Tg for providing the mechanical strength to the final film. During film drying, the material experiences a sequence of transformations, involving water loss, particle deformation, and interparticle coalescence. Depending on the drying conditions, the formulation, and the thickness of the coating, the films may suffer number of shrinkage cracks, which compromises the mechanical integrity of the film. Therefore, Understanding the evolution of the film formation stresses will provide manipulation and control over the film-formation process. In the present research, the effect of particles size and layer thickness on the film mechanical properties and cracking phenomena were studied. The film induced stresses during drying were estimated using WAXS and Beam bending techniques. Moreover, a physical mechanical finite element mathematical model was developed to predict the induced stresses through deformed two particles during drying process.

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Your notes:

Fully bio-derivable CO₂ fixating polymers for HNIPU applications

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Non-isocyanate polyurethanes (NIPUs) are phosgene and isocyanate-free alternatives to standard industry polyurethanes. They are easily accessible from cyclic carbonates and amines. NIPUs and corresponding hybrid materials (HNIPUs) which are derived from epoxy resins partly modified with cyclic carbonates, hold an interesting promise of innovation as they in part show superior mechanical and chemical properties. However, finding an easy process remains a hurdle in NIPU synthesis as long reaction times and rather harsh reaction conditions are required.[1] A route involving polybutadiene (PBD) as a starting material for the sequence of post-functionalization of epoxidation, cyclic carboxylation, and diamine cross-linking could have an interesting potential as a future-proof/green route of routinely synthesizing HNIPUs.[2] Here it is reported how several low molecular polybutadiene were partial epoxidized and how a consecutive carboxylation with CO₂ can be achieved. This particular way of evolving polybutadienes allows for tailored HNIPU preparation; various functionalities are introduced onto the polymer backbone. We have tested a set of metal-free catalysts including conventional, widely used tetra-n-butylammonium bromide (TBAB) for CO₂ insertion reactions into partly epoxidized PBDs optimizing conditions to target quantitative conversions and high selectivities. Eco-friendly NIPU cross-linking reactions with (bio-derivable) diamines further exemplified the capability of polybutadienes in forming a backbone of a tunable, potentially fully sustainable hybrid NIPU thermoset.

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Your notes:

High Barrier Waterborne Polysulfide Dispersions

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Today, the polymer industry is going through significant changes in priorities driven by the growing awareness of ecological issues. In this context, the development of eco-efficient and sustainable processes and products has become an absolute necessity.

As an example, many industrial coating processes involve the use of waterborne products obtained by polymerization in dispersed media. These VOC-free polymer products are indeed a greener alternative to the traditional solvent borne coatings, as water is used as the disperse phase. Although the market of waterborne coatings is constantly increasing, the variety of polymer dispersions commercially available is restricted and relies mainly on chain growth radical polymerization using thermal or redox radical initiator. Hence, the development of polymerization technologies to expand the range of products and to make the process even more efficient and environmental friendly is needed. To answer to this need, we propose an approach that unite a photopolymerization in dispersed media technique with thiol-ene step-growth radical processes to produce polysulfide aqueous dispersed products.

Thiol-ene chemistry has been widely studied, and its application in coating has recently emerged [1] because of its numerous advantages such as rapid kinetics, control of the polymer architecture, and insensitivity to oxygen. [2] Thiol-ene photopolymerization has been used in UV-cured coating formulations [1], although its application is restricted to surface and thin-layer. Since the last decade, the feasibility of thiol-ene photopolymerization in miniemulsion has been reported [3-6]. While minimising cost and environmental impact because of the lower consumption of energy and the use of a VOC-free process, thiol-ene photopolymerization in miniemulsion turns out to be a privileged mean to obtain high sulfur content products with controlled architecture.

Herein, we present how the polymer architecture in thiol-ene chemistry may be fine-tuned by adjusting the monomer functionalities. For that aim, a wide range of thiol and diene monomers was photopolymerized in miniemulsion. The bifunctional monomers resulted in linear structures prone to form crystalline domains within the polymer films, whereas, more than two functional groups per monomer molecule promoted controlled branching and cross-linking and network formation. This could pave the way to a new portfolio of polysulfide coatings, with versatile properties implied by the structure of polymers.

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Your notes:

Determination of micromixing efficiency in viscous media

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Mixing, especially micromixing processes, have an influence on the yield, selectivity and quality of the final product.^[1] After determining the micromixing efficiency, the design of chemical reactors, impeller geometries and the operation conditions can be improved in order to obtain a high yield and a high selectivity of a desired product. One of the most common chemical test reaction is the Villermaux-Dushman reaction containing a neutralization reaction in a borate buffer and a comproportionation reaction yielding iodine due to the injection of an acid. While carrying out this reaction in water is simple, straightforward, and well established, the determination of the micromixing efficiency in higher viscosities is challenging. On the one hand, a suitable viscous media has to be selected and on the other hand, a compatible test reaction has to be found to operate in the selected viscous media.

A high concentrated sucrose solution has been applied, as it is a Newtonian fluid, which can achieve viscosities up to 1200 mPas. The borate buffer was replaced with a phosphate buffer giving two major advantages. Firstly, the handling of the chemical compounds was safe by abstaining from boric acid and secondly the buffer could be completely dissolved in concentrated sucrose solution. Initially, experiments were carried out in a stirred tank reactor yielding the segregation index as a function of the stirring speed at different viscosities using a sucrose solution. Furthermore, the results were transferred into a continuous tubular reactor, where the micromixing efficiency was also determined. Finally, an invert sugar solution was successfully tested as a viscous media for the test reaction with the advantage of reaching viscosities up to 15000 mPas. The result of these experiments highly suggests that sugar solutions can be used as a viscous media to determine the micromixing efficiency at different viscosities.

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