



Conference Guide



Working Party on Polymer Reaction Engineering

9th PhD-Workshop on Polymer Reaction Engineering

23rd November to 25th November 2021 (online event)









Welcome to the 9th 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 ninth time now. It has been launched in Lyon in 2012 with a total number of 35 participants. In 2019, we recorded a number of 49 registrations in Hamburg. Due to the pandemic, no workshop was held in 2020. For 2021, we decided to temporarily switch to an online format in order to provide PhD students with an opportunity to present their work. The next workshop is already in planning and will be held face-to-face in San Sebastian Spain from April 20th to 22nd 2022.

As always, this year's topic are excitingly diverse:

- 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!

Organizing Committee –

Prof. Dr. Markus Busch	Chair of WPPRE, TU Darmstadt
Dr. Kristina Zentel	Secretary of WPPRE, TU Darmstadt
Laura Euler Bueno	TU Darmstadt
Elisabeth Nowottny	TU Darmstadt

Sponsors

Due to the temporary switch to an online format, no "classic" sponsoring of social events takes place this year.

Nevertheless, we are happy to welcome industry representatives from Wiley-VCH, Hungenberg Consultant, Evonik, DSM, Sabic, BASF, Wacker, Sulzer and Arlanxeo to this year's workshop.

Despite the special circumstances, we are delighted and want to warmly thank Wiley-VCH for sponsoring a best contribution prize for the online event!



Program by Days Tuesday, 23rd November 2021

13:00 - 13:10	Prof. Dr. M. Busch, Dr. Kristina Zentel Welcome		~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
13:10 - 13:15	Elisabeth Nowottny (TU Darmstadt) Technical notes on presentation session	14:30 - 15:15	Poster session
~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Session I: Inline Spectroscopy Chair: Elisabeth Nowottny (TU Darmstadt)	15:15 -15:35	Break
13:15 -13:35	<b>Stephanie Schlappa</b> (University of Potsdam) Inline monitoring of nanosized polymer materials using Photon Density Wave spectroscopy	15:35 - 16:05	Introduction of industry representatives
13:35 - 13:55	<b>Laurence Jacob</b> (University of Hamburg) Inline monitoring of latex-particle size distribution in emulsion polymerisation process	16:05 - 17:05	Social event
13:55 - 14:10	<b>Elisabeth Nowottny</b> (TU Darmstadt) <i>Technical notes on breaks and poster sessions</i>	17:05 - 17:10	Elisabeth Nowottny
14:10 - 14:30	Break	~~~~~~~~~~~	Fui c w c ii

this schedule refers to central european time



# Program by Days Wednesday, 24th November 2021

12.00 12.0E	Louro Eulor Ruono	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
13:00 - 13:05	Welcome	15:30 - 15:50	Break
	Session II: Waterborne Coatinas	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Session III: Modelling
~~~~	Chair: Isabel Kronshorst (TU Darmstadt)		Chair: Jonas Degenkolb (TU Darmstadt)
13:05 - 13:25	Sumi Murali Nair (University of the Basque Country)	15:50 -16:10	Stefan Welzel (University of Stuttgart)
of waterborne polymer dispersions	of waterborne polymer dispersions		the radical polymerization of N-Vinylpyrrolidone
13:25 - 13:45	Elvis Lopes Brito (University of the Basque Country) <i>Film Formation of Core-Shell Latex Particles</i>	16:10 - 16:30	Andreas Feuerpfeil (TU-Clausthal) Monte Carlo simulation of non-isothermal semi-batch
13:45 - 14:05	Sheraz Tariq (University of the Basque Country) Study of the inter-particle crosslinking reactions in		vinyl acetate polymerization under industrial important conditions
	waterborne coatings	16:30 - 16:50	Elisabeth Nowottny (TU Darmstadt)
14:05 - 14:25	Hesham Abdeldaim (University of the Basque Country) Soft Core-Hard Shell Latex Particles for Cracking Free Thick Polymer Coatinas	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Copolymerization of Ethylene and Vinyl acetate
~~~~~~		16:50 - 16:55	<b>Dr. Kristina Zentel</b> Farewell
14:25 - 14:45	Break		

16:55 - 18:30 optional get-together on wonder.me

14:45 - 15:30 Poster session



# Program by Days

# Thursday, 25th November 2021

13:00 - 13:05	Elisabeth Nowottny	
	Welcome	

	Session IV: I	Processes	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
Chair: I	ena Gockel	(TU Darm	stadt)

- 13:05 -13:25 **Daniela Eixenberger** (Hamburg University of Technology) Smart Reactors - Surface Enhancement of Additively Manufactured Structures by ARGET ATRP
- 13:25 13:45 **Jana Sklenářová** (UCT Prague) How to increase the Selectivity of the Triboelectric Separation of Plastic Waste?
- 13:45 14:05 **Wasif Razzaq** (University of Strasbourg ) Microfluidic-Assisted Synthesis of Polymeric Microfibers
- 14:05 14:25 **Vida Gabriel** (University of Ottawa) Incorporating Carboxylated Cellulose Nanocrystals in Latexes for Adhesive Applications: A Sticky Situation

14:25 - 14:45 Break

14:45 - 15:15 **Poster session** 

### 15:15 -15:35 Break

- **Session V: solution polymerization & thermodynamics** Chair: Jana Sartorius (TU Darmstadt)
- 15:35 -15:55 **Isabel Kronshorst** (TU Darmstadt) Method for the Determination of Reactivity Ratios at High Conversions in the Continuous Solution Polymerisation Process
- 15:55 16:15 **Jakub Klimošek** (UCT Prague) Experimental and Theoretical Study of Small Hydrocarbons Diffusion in Semi-Crystalline Polyolefins
- 16:15 16:35 reserved presentation slot to be announced

16:35 -16:55 Break

- 16:55 17:00 **Dr. Kristina Zentel & Dr. Stefan Spiegel** (Wiley) Best contribution prize
- 17:00 17:05 **Dr. Shaghayegh Hamzehlou** Information on San-Sebastian workshop
- 17:05 17:15 **Prof. Dr. Markus Busch, Dr. Kristina Zentel** Farewell



# **List of Posters**

poster	poster title	author
1	Radical polymerization of styrene in presence of recycled tires powder: experimental strategy for hybrid machine learning/phenomenological modeling	<u>C. Trinh</u> , B. Lamari, D. Meimaroglou, S. Hoppe
2	Modeling of Copolymer Topologies in High-Pressure Ethylene Copolymerizations in 3D-Space	<u>J. Kirsch</u> , A. Weber, M. Busch
3	Impact of induced condensing agents on comonomer incorporation and polymer properties	<u>N. B. Ishola</u> , F. N. Andrade, T. F.L. McKenna
4	Investigations of Mixing Behavior of Polymerization Processes	L. Ständecke, L. Dietrich, M. Busch
5	Kinetic of Peroxide Decomposition considering the Impact of Solvent, Pressure and Peroxide Cocktail	J. Sartorius, S. Albus, M. Busch
6	Analyses of polyacrylates using electrospray mass-spectrometry and multi-angle-laser-light- scattering (MALLS)	J. Mätzig, M. Drache, S. Beuermann
7	Implementation of an Inline-NIR-Spectroscopy to a High-Pressure System	<u>S. Hintenlang</u> , M. Busch
8	Inline monitoring of nanosized polymer materials using Photon Density Wave spectroscopy	S. Schlappa, M. Krzyczmonik, L. Bressel, M. Münzberg
9	Kinetic investigation of the Dushman reaction for micromixing time calculation	<u>E. Arian</u> , W. Pauer
10	Visualization of Relief Phenomena in High-Pressure Systems	<u>A. Röblitz</u> , M. Busch,



## **Book of Abstracts**

Jana Sklenářová

Isabel Kronshorst

Jakub Klimošek

Julian Kirsch

**Elias Arian** 

14.

15.

17.

- 1. Stephanie Schlappa 13.
- 2. Laurence Jacob
- 3. Sumi Murali Nair
- 4. Elvis Lopes Brito 16. Cindy Trinh
- 5. Sheraz Tariq
- 6. Hesham Abdeldaim 18. Niyi Ishola
- 7. Stefan Welzel 19. Laura Ständecke
- 8. Andreas Feuerpfeil 20. Jana Sartorius
- 9. Elisabeth Nowottny 21. Jonas Mätzig
- 10. Daniela Eixenberger22.Sascha Hintenlang
- 11. Vida Gabriel23.
- 12. Wasif Razzaq24.Aaron Röblitz

#### Inline monitoring of nanosized polymer materials using Photon Density Wave spectroscopy

S. Schlappa, M. Krzyczmonik, L. Bressel, M. Münzberg

University of Potsdam, Institute of Chemistry/Physical Chemistry - innoFSPEC, Am Muehlenberg 3, 14476 Potsdam, Germany

Inline monitoring of the synthesis of polymer dispersions is a frequently discussed topic in research. Due to the high volume fraction and high turbidity of the dispersions undiluted inline monitoring of the synthesis is still challenging but can be approached by Photon Density Wave (PDW) spectroscopy [1]. PDW spectroscopy is a measurement technique for the independent determination of the absorption coefficient  $\mu_a$  and the reduced scattering coefficient  $\mu_s'$  of highly turbid samples. PDW spectroscopy uses intensity modulated laser light, guided via optical fibers into samples with volume fractions up to 60 or even 70 wt-% of particles or other scattering material [2]. Inline measurements are achieved using a small 2.5 cm diameter probe, which is robust against fouling and allows for non-destructive analysis during the process directly through a reactor inlet. The direct inlet of the probe guarantees real-time access to the optical process parameters. Using Mie-theory and the theory of dependent scattering PDW spectroscopy is able to determine particle sizes or size distributions during the reaction process via the reduced scattering coefficient  $\mu_s'$ .

This talk will give insights into PDW spectroscopy and its applications in polymer chemistry. The monitoring of different polymer syntheses via the reduced scattering coefficient  $\mu_s'$  and absorption coefficient  $\mu_a$ , and inline particle growth is presented. Figure 1 shows an example emulsion polymerization process of polyvinyl acetate. The optical parameters determined by PDW spectroscopy show evident polymerization phases and particle growth (not shown in Fig. 1) [3]. Very good agreement of the inline, dilution-free obtained particle size by PDW spectroscopy with offline dilution based light scattering techniques and optical imaging is achieved. Interpretation of the optical properties concerning polymerization phases and particle size scattering and control of the product properties like particle size, particle size distribution and optical properties of the product.



Figure 1: Inline monitoring of the synthesis of a highly concentrated (≈49 wt-%) aqueous disperion of nanometer sized polyvinyl acetate particles via the scattering (red) and absorption (blue) properties using PDW spectroscopy [3].

[1] Bressel, L.; Hass, R.; Reich, O. Particle Sizing in Highly Turbid Dispersions by Photon Density Wave Spectroscopy. *Journal of Quantitative Spectroscopy and Radiative Transfer*, **2013**, *126*, 122–129. https://doi.org/10.1016/j.jqsrt.2012.11.031.

[2] Hass, R.; Muenzberg, M.; Bressel, L.; Reich, O. Industrial Applications of Photon Density Wave Spectroscopy for In-Line Particle Sizing. *Applied Optics*, **2013**, *52* (7), 1423. https://doi.org/10.1364/A0.52.001423.

[3] Schlappa, S.; Brenker, L. J.; Bressel, L.; Hass, R.; Münzberg, M. Process Characterization of Polyvinyl Acetate Emulsions Applying Inline Photon Density Wave Spectroscopy at High Solid Contents. *Polymers*, **2021**, *13* (4), 669. https://doi.org/10.3390/polym13040669.

Your notes:

Session I

#### Laurence Jacob, Werner Pauer

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

The mean particle size and particle size distribution in emulsion polymerisation is still usually determined by offline analysis in diluted solutions. Interfering with the process to acquire a sample can falsify the results and lead to unwanted changes in the reaction. An inline measurement method could be more precise and less subject to problems. New investigations regarding the inline measurement method of photon density wave (PDW) spectroscopy^[1] were performed to explore its suitability for inline particle size measurement in high solid content emulsion polymerisation. The objective of the experiments was to determine whether offline methods such as dynamic light scattering (DLS) and sedimentation analysis, by means of disc centrifuge, could be replaced by PDW spectroscopy. To do so, a series of high solid content emulsion copolymerisations of vinyl acetate and Versa® 10 were carried out in different reactor sizes, going up to 100 L. The emulsifier content was varied to target different particle sizes, achieving a size range of 50 to 325 nm. The reactions were carried out in a semi-batch process, using a redox initiator system, consisting of L-ascorbic acid, tert-butyl hydroperoxide and ammonium iron (III) sulfate. The results of the different methods were plotted against each other. The overall results of the method comparison showed a slope of (0.94 ± 0.06) and a correlation guality of 98% for the linear fit comparing PDW spectroscopy with a disc centrifuge, and a slope of  $(0.99 \pm 0.14)$  and a correlation quality of 92% with DLS. The results seem very promising regarding the correctness of the PDW spectroscopy measurements and the suitability of PDW spectroscopy was proven experimentally with a polymer content of up to 63 wt%. [2]

^[1] L. Bressel, J. Wolter, O. Reich, J. Quant. Spectrosc. Radiat. Transf. 2015, 162, 213–220.

^[2] L. I. Jacob, W. Pauer, RSC Adv. 2020, 10, 26528–26534.

Your notes:

<u>Session I</u>

#### Use of zwitterionic monomers for colloidal stabilization of waterborne polymer dispersions

<u>S.Murali¹</u>, A.Agirre¹, R. Tomovska² ¹POLYMAT, Institute for polymer materials , University of the Basque Country UPV/EHU, Avenida Tolosa 72, 20018 Donostia-San Sebastián (Spain). ²IKERBASQUE, Basque Foundation for Science, , Maria Diaz de Haro 3, 48013 Bilbao, Spain

Waterborne latex dispersions have huge application possibilities, starting from adhesives and paints, up to biomedical applications.¹ These high solids content dispersions are usually produced by emulsion polymerization using surfactants. Surfactants are instrumental in particle nucleation, they stabilize the system during the reaction process and maintain the stability during storage and transport as well as in formulated products. However, since surfactants are not chemically bonded to the polymer particles, during film formation they can migrate onto the film surfaces, which brings undesired film properties and negative impacts on the environment¹.

Incorporation of charged moieties to the polymer backbone by copolymerizing minor amounts of ionic monomers with the main monomers has shown to be a good strategy to produce surfactant-free latexes² with excellent colloidal stability and improved performance. Following this strategy, in this work zwitterionic monomers were selected to provide stability to the polymer dispersions. Zwitterionic monomers are monomers that consist of the same number of oppositely charged cationic and anionic groups, thus their overall charge is neutral. Among others, polyzwitterions exhibit antifouling and antipolyelectrolyte properties, therefore, it was expected that zwitterionic monomers would impart not only colloidal stability, but as well novel properties and widen the application possibilities.³

For that aim, in the present work, different zwitterionic monomers were selected and copolymerized with methyl methacrylate and n-butyl acrylate by seeded semi continuous emulsion polymerization. The performance of the produced surfactant free coatings were compared with a latex stabilized using conventional surfactant. As expected, the latexes stabilized entirely with the zwitterionic monomers presented enhanced properties with respect to the latex stabilized with the conventional surfactant.

[1] Aramendia, E., Mallegol, J., Jeynes, C., Barandiaran, M.J., Keddie, J.L., Asua, J.M. Langmuir, 2003, 19, 3212-3221

[2] Bilgin, S., Tomovska, R., Asua, J.M European Polymer Journal, 93 2017 480-494
 [3] Laschewsky, A. Polymers, 2014, 6, 1544-1601.



#### Film Formation of Core-Shell Latex Particles

#### Elvis Lopes Brito (a), Nicholas Ballard (a,b)

#### a) POLYMAT and Departamento de Química Aplicada, Facultad de Ciencias Químicas, University of the Basque Country UPV/EHU, Joxe Mari Korta zentroa, Tolosa Hiribidea 72, Donostia-San Sebastián 20018, Spain

#### b) Ikerbasque, Basque Foundation for Science, 48013 Bilbao, Spain

The presence of volatile organic compounds (VOCs) in conventional solventborne coatings and their negative environment impact has motivated the development of alternative waterborne systems [1]. A major feature that distinguishes waterborne systems from their solventborne counterparts is the film formation process. As a film-forming latex dries, it is transformed from a colloidal dispersion into a continuous polymer film [2]. The quality of the fused film, in combination with the bulk polymer character, determines the ultimate coating properties. Consequently, an understanding of the process of film formation is critical for the development of latex coatings. In this work, we explore the film formation behavior of core shell latex particles. Firstly, a series of hard-core/soft-shell latexes (M1) was prepared and their film formation behavior in terms of the hard/soft phase fraction and particle size distribution was evaluated. We explore the limits in which the presence of the hard phase compromises the formation of a continuous film using MFFT measurements and tensile tests.



**Figure 1** – (Left) Comparison of MFFT of the multiphase latex particles with low Tg shell polymer (M1) and higher Tg shell polymer (N1) as a function of relative volume of the hard non-deformable core. (Right) Tensile properties of the films prepared using N1 with different shell fractions

[1] Jiang, S.; Van Dyk, A.; Maurice, A.; Bohling, J.; Fasano, D.; Brownell, S. Design Colloidal Particle Morphology and Self-Assembly for Coating Applications. Chem. Soc. Rev. 2017, 46 (12).

[2] Keddie, J. Film Formation of Latex. Mater. Sci. Eng. R Reports 1997, 21 (3), 101–170...

#### Your notes:



#### Session II

#### Study of the inter-particle crosslinking reactions in waterborne coatings.

Your notes:

#### Sheraz Tariq, Maria Paulis

#### POLYMAT Institute for Polymer Materials, University of the Basque Country UPV/EHU, Avenida Tolosa 72,20018 Donostia-San Sebastián (Spain)

Waterborne two-component binder systems are already commercially available for a long time as they were introduced onto the market in the early 1990s. One of the components acts as crosslinker, in order to produce hard and strong films. Due to some environmental restrictions, low molecular weight crosslinkers are under scrutiny. Therefore, one alternative way to overcome these concerns would be to change the crosslinking chemistry or to work with non-oligomeric two-component systems. In the latter case, the reactive functional groups would be attached to two different polymer particles.

We have followed such approach by using the crosslinking reaction between acetoacetoxy ethyl methacrylate (AAEMA) and amine functionalities [1]. Therefore, component-1 latex was prepared with AAEMA functionality and component-2 latex with amine groups in the shell.

The crosslinking in blends of component-1 and component-2 latexes during the film formation has been investigated by preparing latexes with 5 wt% of AAEMA, and following the tensile strength, MEK double rub test, FTIR spectroscopy, rheological measurements and microscopy analysis of the film. First, the crosslinking chemistry was applied in the system having similar particle size and same monomer composition. The annealing effect was also investigated by studying the properties of the resultant film, by drying the film initially at room temperature and then annealing it at 60 °C for one day

In order to further explore the crosslinking system, different variables such as the glass transition temperature (Tg) and particle size (dp) of the different components in the blend were also studied. In fact, the system having different particles size and Tg showed better final film properties than the system containing the same particle size and monomer composition in both components.

 M.J. Collins, J.W. Taylor, Stable amino-containing polymer latex blends. U.S. Patent 5,998,543 (1997).

#### Session II

#### Soft Core-Hard Shell Latex Particles for Cracking Free Thick Polymer Coatings

#### Hesham Abdeldaim, José M. Asua

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#### Hesham.abdeldaim@polymat.com, Jm.asua@ehu.es

Due to environmental reasons, the coatings market is shifting from solvent-borne to waterborne polymers. The main hurdle to be overcome in this transition is the so-called film forming paradox of the waterborne coatings that refers to the need of achieving at the same time easy film formation at room temperature (that requires a low Tg polymer) and strong mechanical properties (that need high Tg). Traditionally, this has been achieved by using coalescent agents that plasticize the polymer during the film formation and later evaporate leaving a hard film. However, the use of coalescent agent is under scrutiny as it is a VOC that is released to the environment. One alternative found by the coating manufacturers has been to use heterogeneous particles comprising hard and soft polymers. Among the different particle morphologies, the soft core-hard shell structure gives the best balance. The hard shell forms a honeycomb structure that provides excellent mechanical properties. However, during the formation of the film, the hard shell should be deformed and this creates stresses in the film. The stresses increase with the thickness of the film leading to the formation of cracks.

In this presentation, the mechanisms of cracking formation during film drying will be unveiled combining carefully design experiments and mathematical modelling. It will also shown how this knowledge can be used to develop strategies to avoid cracking and enhance the mechanical integrity of the film while having a low minimum film forming temperature.

Fouling in continuously operated tubular reactor for the radical polymerization of N-Vinylpyrrolidone

#### <u>S. Welzel</u>, U. Nieken University of Stuttgart, Institute of Chemical Process Engineering, Böblinger Straße 78 70199 Stuttgart

Specialty polymers such as Polyvinylpyrrolidone (PVP) are mainly produced in batch or semi-batch operated tank reactors. The advantage of this process types is its robustness and flexibility. To produce consistent product quality, lower maintenance costs and better energy efficiency, continuous reactor systems have been considered as alternative. Especially, tubular reactors with mixing elements are of interest to manage low-volume products. A serious problem of continuous operation in mixer-reactors is the formation of fouling deposits which can result in blocking and shutdown of continuous reactors.

A prerequisite to formation of fouling deposits and wall layers are side reactions which produce high molecular weight, branched, or even crosslinked polymer chains.[1] The formation of these polymers (gel formation) occurs preferably in dead zone behind mixing elements as well as close to the wall. The locally increased residence time in such regions increase the impact of side reactions. Formation of a viscous layer at reactor walls or dead-zones changes the flow pattern, leads to large cross-sectional concentration gradients and amplifies diffusive mass transport of monomer. As large and branched polymer chain can hardly "escape" from the viscous regions due to low diffusion velocity, a highly viscous layer is built up. Such behavior has been reported for polymerization in tubular reactors, for example [2],[3],[4],[5].

The polymerization kinetic of N-vinylpyrrolidone (NVP) has been extended by side reactions. Formation of terminal double bounds was identified as the cause of high molecular, branched polymer [1]. The number of terminal double bonds are modeled with a pseudo-distribution approach and the chain length is solved directly in the original model. The proposed mechanisms has been validated against experimental data from continously operated stirred tank reactors [6]. For CFD implementations, the original two dimensional model was reduced to a zero dimensional moment model on all discrete property coordinates to reduce the numerical effort.

To investigate the interplay between hydrodynamics, diffusive mass transport and reaction kinetics we conducted CFD simulations in tubular reactors without mixing elements and carefully compared model predictions to a comprehensive set of experiments.

The polymer properties are represented by their moments. If the diffusion coefficients for polymer, monomer and solvent are identical, transport equations for moments can be derived easily. This is here not the case. It is essential to consider the low mobility of polymer chains compared to monomer and solvent. Therefore, we used a new approach based on Maxwell-Stefan diffusion. The transport equations of moments now account for low mobility of polymer chains and high mobility of solvent and monomer. In addition, we implemented an increasing concentration-dependent viscosity. The model has been implemented into the open-source package Openfoam[®]. CFD simulations predict the formation of a highly viscous wall layer in a tubular reactor, which strongly depends on monomer and initiator concentration and on flow velocity.

To validate model predictions a capillary reactor was set up and the residence time distribution of experiments and CFD predictions were compared.

To determine the residence time experimentally, a salt solution was used as a tracer and measured with a conductivity cell at the inlet and outlet of the reactor. To achieve a pulsed-shaped inlet signal, a HPLC switching valve with a sample loop was used to inject the tracer.

Different experiments with varying monomer and initiator concentrations are carried out to validate the model predictions in a wide range of conditions.

An example of CFD simulations is shown in Figure 1, which presents the polymer weight fraction of different monomer concentrations after 100min of reaction time. An increase of monomer and initiator concentration causes the occurrence of a smaller layer. Simultaneously, the starting point for the formation of the wall layer can be observed with greater axial distance from the inlet. The formation of wall deposits changes the shape of the residence time distribution. The viscous layer leads to a faster breakthrough of the tracer impulse and a strongly increased tailing, which is in accordance with experimental findings.



Figure 1: Polymer weight fraction for different monomer feed concentrations after 100min of reaction time.

- P. Deglmann, M. Hellmund, K. Hungenberg, U. Nieken, C. Schwede, and C. Zander, "Side Reactions in Aqueous Phase Polymerization of N -Vinyl-Pyrrolidone as Possible Source for Fouling," *Macromol. React. Eng.*, p. 1900021, Aug. 2019.
- [2] M. Hellmund, "Kinetik und Modellierung der kontinuierlichen Polymerisation von N-Vinylpyrrolidon," University of Stuttgart, 2020.
- [3] S. Fries, D. M. Castañeda-Zúñiga, J. Duchateau, P. Neuteboom, C. T. Porras, and M. Busch, "Fouling in the High Pressure LDPE Process: Experimental and Computational Investigation Approach," *Macromol. Symp.*, vol. 360, no. 1, pp. 78–86, 2016.
- [4] M. F. Cunningham, H. K. Mahabadi, and K. F. O'Driscol, "Bulk polymerization in tubular reactors iii. Modelling fouling behaviour," *Polym. React. Eng.*, vol. 1, no. 2, pp. 245–287, 1993.
- [5] S. Fries, "Modelling of Fouling Mechanisms in the LDPE Synthesis," Technical University of Darmstadt, 2019.
- [6] C. Zander, K. D. Hungenberg, T. Schall, C. Schwede, and U. Nieken, "Modeling Strategies for the Propagation of Terminal Double Bonds During the Polymerization of N-Vinylpyrrolidone and Experimental Validation," *Macromol. React. Eng.*, vol. 14, no. 3, 2020.

Session III

#### Monte Carlo simulation of non-isothermal semi-batch vinyl acetate polymerization under industrial

important conditions

<u>Andreas Feuerpfeil¹</u>, Marco Drache¹, Laura-Alice Jantke², Timo Melchin², Jessica Rodríguez-Fernández², Sabine Beuermann^{1*} ¹ Clausthal University of Technology, Institute of Technical Chemistry, Arnold-Sommerfeld-Straße 4, 38678 Clausthal-Zellerfeld, Germany ² Wacker Chemie AG, Johannes-Hess-Str. 24, 84489 Burghausen, Germany

Poly(vinyl acetate) is an important polymer for industry and daily life. Optimizing the polymerization process and the product requires a deep knowledge of the reaction system and the microstructure of the product. Monte Carlo simulations (statistical approach) provide a much higher level of detail compared to deterministic methods. Microstructural information of individual virtual polymer molecules is availabe and can be analyzed or subsequently simulated.

To obtain realistic virtual polymers, the polymerization process is required to be simulated as realistically as possible. For this purpose, the focus is on the kinetic model.

The kinetic model presented is mainly based on kinetic coefficients known from literature. In addition, a chain length- and solids content-dependent termination model for vinyl acetate is developed. The model was validated with an experimental data set of widely varying industrial important conditions: non-isothermal, in solution, semi-batch, under reflux, up to a high degree of solids content and full conversion.

With respect to modeling two challenges occur: First, the continuously increasing control volume due to the semi-batch mode. Second, the continuously changing reaction mixture composition resulting in a change of the boiling point, and thus, a change of the temperature. The kinetic model developed provides a very good representation of the experimental data for widely changing reaction conditions, which demonstrates the robustness of the model.

#### Your notes:

Session III

#### Development of a Model for the Free-Radical High-Pressure Copolymerization of Ethylene and Vinyl

Your notes:

#### acetate

<u>Elisabeth Nowottny</u>, Technische Universität Darmstadt, Darmstadt, Germany; Markus Busch, Technische Universität Darmstadt, Darmstadt, Germany

Due to their high versatility and ease of processing polymeric materials have outgrown most humanmade materials with a production of 368 million tons in 2019.^[1,2] An example for a widely applicable copolymer is polyethylene-vinyl acetate (EVA). EVA holds a diverse spectrum of materials with a broad range in applications.^[3] Due to the complex structure-property-relationship regarding suitable applications, modeling the process of EVA production is a topic interesting to both industry and academia. This work presents an effort of deriving a valid deterministic model based on the kinetics of copolymerization, which is applicable in depiction of the polymerization process.

Hereby, a new set of temperature and pressure dependent kinetic coefficients for the free-radical polymerization of vinyl acetate was derived from published data. The acquired Arrhenius parameters (preexponential factor and activation energy) are classified via confidence contours in parameter space. The determined ellipses are based on a self-developed geometric covariance approach, which has been validated to yield identical results as the well-known sum-of-squares method published by van Herk.^[3] The newly developed approach of this work has the advantage to merely rely on basic software such as Microsoft Excel, so no programming is needed to determine confidence contours.

Via appliance of a working group validated set of ethylene free-radical polymerization kinetics^[4] and the newly developed set of vinyl acetate kinetic coefficients, a copolymerization model is built in the modeling software Predici[®]. A strategic set of mini-plant experiments was conducted to validate the kinetic coefficients in regard of matching the experimental molar mass distribution.

[1] Plastics Europe, Plastics – the facts 2020.

[2] Nayak, S. et al., Trends and Applications in Advanced Polymeric Materials, Wiley, 2017.
[3] Henderson, A., IEEE Electrical insulation magazine, 9(1), 30-38, 1993.
[4] van Herk, A., Journal of Chemical Education, 72(2), 138, 1995.
[5] Busch, M., Macromol. Theory Simul., 10, 408-429, 2001.

#### Your notes:

Session III

#### Incorporating Carboxylated Cellulose Nanocrystals in Latexes for Adhesive Applications: A Sticky Situation <u>Vida A. Gabriel</u>, Marc A. Dubé University of Ottawa, Department of Chemical and Biological Engineering, 161 Louis Pasteur Pvt., Ottawa ON, K1N 6N5, Canada

Pressure-sensitive adhesives (PSAs) are polymeric materials, which can adhere to a surface with a light touch and be removed without leaving a residue (e.g., masking tape or Post-itTM notes). Emulsion polymerization is a more sustainable approach to producing PSAs because it utilizes water as the continuous phase as opposed to the toxic and polluting solvents used in solution polymerization or hot melt-processing, for example.[1] In the last few decades, nanocellulosic materials, like cellulose nanocrystals (CNCs), have gained popularity as nanofillers due to their low toxicity, renewability, and abundance. CNCs can be incorporated in latexes in-situ – a preferable method to ex-situ addition because it ensures latex homogeneity and better performance enhancements. Even in the smallest quantities (<1%), CNCs can significantly improve the mechanical strength of polymeric materials.[2]

DextraCel[™] is a new type of CNCs produced by a Canadian start-up, Anomera Inc, with carboxylic surface groups (henceforth referred to as "cCNCs"). Anomera produces their cCNCs in two forms: a 4.5 wt.% slurry in water, and a spray-dried powder. The interactions between cCNCs and other standard latex components are studied and reveal that they behave differently than the more common sulfated CNCs. Specifically, cCNCs are sensitive to the ionic strength of the aqueous phase and therefore, a more creative approach to emulsion polymerization was undertaken to produce nanocomposites latexes. The classical seeded semi-batch emulsion polymerization procedure was modified; instead of using the traditional anionic surfactant and initiator in the seed stage and the feed stage, a classical polymer seed was formed (with anionic surfactant and initiator) and an unconventional feed was used which had nonionic surfactant and a monomer-soluble initiator.[3] Doing this preserved a low ionic strength of the latex, which ensured the cCNCs stability throughout the reaction. Because the dispersion method of nanocellulose is crucial to good latex performance, both the wet and dry cCNCs were dispersed in various ways and incorporated in-situ to study the effects of dispersion method and loading on the latex adhesive properties. The resulting nanocomposite films showed substantial improvements to the three key adhesive properties, peel strength, tack, and shear strength, regardless of dispersion method. Relative to a blank latex (produced without cCNC), films cast from a latex containing only 0.5 wt.% of the wet cCNCs (relative to monomer) demonstrate 26x higher peel strength, 4.5x greater tack, and 7.7x longer shear strength. Atomic force microscopy (AFM) was performed on the PSA films and images revealed that the cCNCs promote particle coalescence and film formation. Unlike sulfated CNCs, cCNCs' can stack side-by-side and head-to-tail to form fibre-like structures, rendering their 'apparent' aspect ratio – a key factor in polymer matrix reinforcement – higher than their true aspect ratio.

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Your notes:



Session IV

#### Smart Reactors - Surface Enhancement of Additively Manufactured Structures by ARGET ATRP

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To fulfil the demands of future industry, smart reactors are essential. Therefore, additive manufacturing is a very promising technology, as it enables the production of tailor-made structures in a fast and cost-effective manner [1]. When applied in packed bed reactors, these structures can be designed in a heat and mass transfer enhancing manner, hence, to improve the efficiency of the whole process [2].



Figure 1 Packed bed reactor with additively manufactured packing. Surface enhancement by stimuli responsive polyacrylic manufactured material, an application as heterogeneous biocatalyst support is uneconomic. To enable a higher surface per volume ratio, ARGET ATRP (Activator ReGenerated by Electron Transfer Transfer Radical Atom Polymerization) is applied for polymer brush synthesis on 3Dprinted material. A schematic overview of the surface enhanced additively manufactured structure, with immobilized enzymes, is shown in Figure 1.

Due to low porosity of the additively

acid brushes including subsequent enzyme immobilization The chosen support material is Nylon 12, as there are trivial surface functionalization procedures known.

Besides FTIR spectroscopy (Fourier Transformation Infrared Spectroscopy), also XPS (X-Ray Photoelectron Spectroscopy) and ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) are performed to determine the covalent binding of initiator to the surface qualitatively and quantitatively. Finally, the attached polymer is analysed via TGA (Thermogravimetric Analysis), SEM (Scanning Electron Microscopy), FTIR and XPS. Figure 2 summarizes the functionalization procedure of a 3D-printed structure to yield surface



Figure 2 Workflow of surface enhancement on additively manufactured structure with subsequent enzyme immobilization

Further optimization of the polyacrylic acid synthesis in free solution is targeted by a response surface plot, using a Box-Behnken Design. Factors accounted for are, the catalyst amount, reducing agent, time and the volume of organic solvent.

Moreover, a correlation between monomer conversion and molecular weight of polymer brushes is of utmost importance, to determine the influence of molecular weight on the residual enzymatic activity. This approach is demonstrated in aqueous media applying a hydrolysis reaction catalysed by the Esterase 2 from Alicyclobacillus acidocaldarius. Finally, the synthesis of stimuli responsive polymer brushes not only tackles the limitation in surface area but moreover, it implements the possibility of an autonomous process control by presence of certain stimuli. For instance, a shift in pH causes a conformational change of the polymer brushes (coil-globule transition) what affects enzyme activity by diffusion limitation. This effect enables an autonomous process control by adapting to continuous changes of process conditions during the reaction progress.

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Your notes:

Session IV

#### How to increase the selectivity of the triboelectric separation of plastic waste?

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Plastic materials find their use in many applications such as packaging, automotive, construction and electronic industry. This produces large amounts of plastic waste, which accumulate in landfills and the oceans. The separation of plastic materials is crucial in the recycling process to produce new high-quality materials, but moreover, separation is important even in incineration, which can be used instead of recycling. By incinerating the plastic waste, we could reduce the large volume of solid waste and we could get energy from the plastics. In other words, we can make from useless and cumulating waste a resource with a positive economic value. However, halogenated plastics (mostly PVC) cause problems during incineration because they can produce toxic gases, including dioxins. Thus, special incineration conditions are required, and then the process becomes more complicated, and incineration is no longer profitable. Therefore, the separation of halogenated plastics could be the first-step solution. Even though many separation techniques are known, they all have significant drawbacks; thus, none can be used universally. In our research, we are focusing on the improvement of efficiency of a triboelectric separation of plastics, which is a method with the potential to become an important member of the recycling chain for many reasons, such as low costs of the separation process, automatization potential, possible separation of black materials etc.

Triboelectric separation is based on the phenomenon that each plastic material obtains a different electrostatic charge by friction contact against a proper counter-material. The basic separation process consists of three main steps. In the first step, plastic waste is grinded into small pieces, in the second step, the charge is generated on their surface. Lastly, the pieces are separated during the free fall between electrodes in the electrostatic separator. The charge is 'generated' on the surface of the pieces during their contact and friction and after their subsequent separation. The amount and direction of the transferred charge are generally determined by the properties of both contacted objects, i.e., grinded waste particle and the charging cell made from a specific counter-material. The selection of a countermaterial is the most challenging task of designing a triboelectric separator, as it plays a key role in the controlling of the charge obtained by individual plastic pieces. The tribocharging of dielectrics or insulators is not well understood yet, although some theoretical or empirical concepts correspond well with experimental results. So even determining a suitable counter-material is not possible. Thus, there is no sufficient knowledge to predict the charging behaviour of such similar materials like plastics when distinguishing between their grades (for example, HDPE and LDPE), and that is why most of the work needs to be done experimentally. Furthermore, the nature of the materials is not the only parameter influencing the direction and magnitude of the transferred charge, but the type of contact of pieces with the counter-material, the properties of the surrounding atmosphere, as well as the dimensions and the shape of the grinded pieces also plays a role.

We use self-constructed charging apparatus based on different contacting approaches: contact during rotational motion, enhanced by vibrations or contact during sliding motion. To evaluate the charge on pieces, we use two methods: we can estimate the total charge in a sample in a Faraday pail connected to the electrometer (used for experiments with pure materials, not mixtures), or we are using our self-constructed free-fall separator to evaluate the charge distribution in the sample. After the separation, plastic pieces are collected in boxes based on the trajectory of their fall in the electric field. Then, the charge of pieces in individual boxes is measured in the Faraday pail. Finally, the representation of different plastic materials in collectors is evaluated.

Our work is focused on improving electrostatic separation by finding proper counter materials to effectively separate multiple-component plastic mixtures by separating one material per cycle and recharging the remaining mixture with different counter materials during each cycle. We compared the most promising tribocharging mechanisms for automatization (rotational and vibrational), and we combined these methods with a corona discharge to decrease the time needed to achieve sufficient, i.e., saturation charge on individual pieces. We performed a study addressing the charging dependent on material composition with 8 cells with different compositions and 9 waste plastic materials, and we showed that the magnitude and, in some cases, even polarity can be controlled by the choice of the cell material and the mode of charging. These results can be used as guidance to choose a suitable material for the efficient separation of various plastic mixtures, as we demonstrated with the separation of

3-component mixtures, aiming for the successful separation of halogenated material – PVC from the mixture, as PVC is inconvenient for incineration. We began with a one-stage separation with high purity of the two materials but in a low yield, and then we introduced the repeating cycle in two different ways. One is to reach higher purity by separating only one material in one stage, and another one aims to increase the yield. Finally, we reached to sort out the PVC with purity up to 91 % at 88% recovery, PET of 77% purity and 64% recovery and completely PVC-free, and PP of 75% purity and 80% recovery with approx. 3 % of PVC.

In our further experiments, we focus on the effect of an external electric field, which can be used to fine-tune the charging of plastic particles during tribocharging. Our results show that with the increasing field strength in the charging cell, we can lower the value of the saturation charge of particles. By controlling the saturation charge of particles by an external electric field, we could decrease the number of charging cells consisting of different materials needed to efficiently separate a mixture of plastic waste and thus, simplify the automatization of the process.

#### Microfluidic-Assisted Synthesis of Polymeric Microfibers

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Microfibers have an excellent potential for biomedical applications such as tissue engineering, wound dressing, cell encapsulation, drug delivery, and microvascular grafting [1]. In recent years, microfluidic spinning has emerged as an outstanding and simple technique for the production of micro- and nanofibers with controllable size and morphology [2]. A 3-dimensional co-axial flow with the core fluid flowing in the center and surrounded by the flow of a miscible sheath fluid, was established in a capillary based microfluidic device. Both fluids come into contact at the exit of the capillary where the shear forces induced by the high flow rate of the sheath flow elongate the core fluid into a continuous thread of small diameter which upon downstream UV irradiations gives rise to a microfiber [3] having a diameter as low as 23 µm. In our work, we have produced microfibers by photopolymerization of tri(propylene glycol) diacrylate (TPGDA) using a simple microfluidic capillary-base device (Fig.1). The impact of various parameters including flow rate ratio  $(Q_c/Q_c)$  and viscosity ratios  $(\eta_c/\eta_c)$  of sheath and core fluids, inner (I.D) and outer (O.D) diameter of capillary and monomer concentration on the diameter of the fibers was investigated. From all the data collected, an empirical correlation was developed which precisely described the fibers diameter as a function of capillary number ratio of sheath to core fluid, capillary inner diameter and monomer volume fraction. This result paves the way to the continuous-flow production of microfibers with well-controlled morphological characteristics.





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#### Your notes:



#### Session IV

#### Method for the Determination of Reactivity Ratios at High Conversions in the Continuous Solution **Polymerisation Process**

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Given today's environmental challenges, intelligent material design is a key to sustainability. Here, both preparation of polymers with targeted material properties and their life cycle can serve as a lever. The continuous solution polymerisation mini-plant is a tool for polymer reaction engineering. It can be used to achieve insight into the industrial catalytic polymerisation process on a small scale. By this, properties can be predicted based on the recipe which saves time and resources in the long run.

The continuous solution polymerisation process is commonly used for the preparation of linear lowdensity polyethylene (LLDPE). LLDPE is a product of the co-polymerisation of ethylene with  $\alpha$ -olefins. The properties of LLDPE are a function of the polymer's micro-structure, in particular chain length ( $P_n$ ), sidechain length, and co-monomer content. The different microstructures that can be varied are shown in Figure 1. For their prediction, it is crucial to understand the interaction of these parameters in polymerisation as they influence each other.



Figure 1.: The variation of different microstructural aspects that result in different polymer properties and how they can be influenced.

To adjust specific properties, the parameters should preferably be systematically changed. To reduce the complexity, the co-monomer incorporation is investigated for one co-monomer.

The behaviour is measured by the determination of reactivity ratios. The ratios are a function of the catalytic system, the used monomers, a possible CTA, and the overall reaction conditions. Therefore, a systematic screening of reactivity ratios at different parameters is crucial for the prediction of microstructure. In the given setup of the mini-plant, the determination of reactivity ratios is based on different feed compositions and the resulting co-monomer content in the polymer. The reactivity ratios are obtained by a non-linear fit of the Mayo-Lewis equation.^[1] This allows the estimation of reactivity ratios without further assumptions than those of Mayo and Lewis. The obtained reactivity ratios are valid for one co-monomer and a defined amount of chain transfer agent. Using this knowledge, in future pattern polymers can be prepared to investigate the influence of short-chain branching. The defined structures can be used to understand the link between microstructure and rheology, thermodynamic aspects of substances in defined environments, or the decomposition of polymer chains under pyrolysis.

We acknowledge the generous support of Borealis AG.

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## Your notes:

Session V

#### Experimental and theoretical study of small hydrocarbons diffusion in semi-crystalline polyolefins

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Transport of monomer(s) is an essential topic in polymer reaction engineering. Studying the diffusion of monomers in complex semicrystalline polymer structures is improving our knowledge about diffusion and relaxation processes. The aim of this work is the high-quality experimental and systematic investigation of diffusion in semicrystalline polyolefins by differential pressure decay method.

Investigation of small molecules gases is performed on our designed differential pressure decay. Chamber with polymer sample is systematically pressurized/depressurized to observe pressure evolution due to sorption/desorption into/out the polymer sample. Repeating of high number of experiments across wide concentration range is time effective due to automated experimental procedure. Each diffusion pressure evolution is then processed to obtain single diffusion coefficient.

The objective of our research is to investigate the transport of light-hydrocarbon molecules in semicrystalline polymers. Polyolefin morphology with stacked crystalline lamellae and the presence of two different amorphous regio

different amorphous regio regions for monomers.



Figure 1: 3D image of semi-crystalline polyethylene. Grey parts represent crystalline phase, red is free amorphous phase and blue is constrained amorphous phase [1].

Recently modified apparatus is providing equal sorption and desorption ethylene diffusion coefficients and thus thermodynamically correct result. In this contribution we are comparing ethylene diffusion in amorphous phase of various density grades PE to demonstrate effect of impenetrable crystalline phase presence at various temperatures. Next goal is the extension of diffusion measurements to larger molecules (e.g., propylene, butene or 1hexene). Sorption isotherms will be measured to calculate volume fraction of penetrant in amorphous phase to compare diffusion coefficients across monomer types. Penetrant volume fraction will be also used for mathematical modelling of diffusion.

Currently we are employing Fickian approach with advanced evaluation program to obtain diffusion coefficients. Disadvantage of this approach is no information about concentration dependency of diffusion coefficient. Free Volume Theory model [2] will be used to interpret concentration dependency of diffusion coefficient and to determine polymer sample fundamental constants.

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Your notes:



### Session V

## Radical polymerization of styrene in presence of recycled tires powder: experimental strategy for hybrid machine learning/phenomenological modeling

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Radical polymerization of styrene in presence of recycled tires powder, also called GTR (Ground Tire Rubber, Figure 1), displays two industrial interests. It allows the recycling of used tires as well as the elaboration of new composites materials with enhanced mechanical properties thanks to the grafting reaction of polystyrene on GTR. The goal of this study is to model this polymerization system in the perspective to better understand the link between process parameters (i.e., reaction temperature, initial amounts of reactants) and the quality of the final product obtained (i.e., styrene conversion, grafting efficiency). However, this system is complex to model with classical phenomenological approaches (based on physics and chemical equations) as a lot of reactions and non-linear phenomena occur simultaneously and their mechanism is not always well known [1]. It is especially the case of the grafting mechanism. Furthermore, commercial GTR is obtained from diverse tires types and has consequently different and unknown compositions, which can have significant accelerating or inhibiting effect on polymerization. Phenomenological models are therefore, for all the aforementioned reasons, quite long to develop and not very precise. Inversely, machine learning (ML) methods, based solely on data, already demonstrated their ability to tackle complex problems in other fields when classical approaches fail or are inefficient. In this study, a hybrid approach is considered in order to combine the strengths of both approaches, namely the explicability of phenomenological models and the precision of machine learning methods. In particular, machine learning will be used to predict the deviation caused by the presence of GTR. which is difficult to formalize.





The poster will focus particularly on the experimental challenges encountered as well as the strategy adopted for generating sufficiently data of good quality (*Figure 2*), these being of prior importance in any machine learning approach.

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Your notes:

<u>poster</u>

#### Modeling of Copolymer Topologies in High-Pressure Ethylene Copolymerizations in 3D-Space

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Low-density polyethylene (LDPE), which is produced via radical polymerization under high pressures and temperatures up to 3500 bar and 300 °C, is characterized by its long-chain branching.^[1] It possesses low temperature impact toughness and impact resistance since the long-chain branches can entangle under stress.^[2] To adapt the properties of LDPE to a specific application, comonomers can be added to the process. In this way, the polymer can be optimized in terms of properties, such as thermal stability or corrosion resistance. In practice, it is hard to determine the position of the comonomer units inside a copolymer structure since this information is not analytically accessible. However, the spatial proximity of comonomer units, especially, if they contain polar side groups, has an influence on the size of the polymer coil and thus on the radius of gyration. Since this is a decisive factor in processability, it is useful to investigate the effect of the comonomers on the copolymer structure. For this purpose, modeling is an important tool for polymer reaction engineering, due to the fact that with an existing model variations can be carried out easily. To provide a proper understanding of the influence of the position of comonomer units on the spatial structure, a hybrid stochastic modeling approach is used.

This work focuses on such a hybrid stochastic approach, which is able to describe the copolymerization of ethylene and an arbitrary comonomer. The chosen reaction apparatus is an isothermal laboratory autoclave with a volume of 100 mL. This is assumed to be ideally mixed, so no concentration and temperature gradients are present. The hybrid approach consists of two successively executed modeling programs. First, a deterministic simulation with the commercially available software Predici[®] which numerically solves a differential equation system is executed. This differential equation system results from the reaction network of the ethylene polymerization. Additionally, reaction frequencies are calculated which provide information about how often each reaction occurs. Afterwards, a statistical simulation using a Monte Carlo algorithm is carried out. Monte Carlo takes the reaction frequencies to simulate an ensemble of molecules using a single molecule approach.

With this approach, it is possible to achieve information about the exact topology of each polymer molecule formed. The obtained topologies can be represented in 3D-space using a 3D-random walker.

We acknowledge the generous support of the Siam Cement Group co. Ltd.

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Your notes:

poster

#### IMPACT OF INDUCED CONDENSING AGENTS ON COMONOMER INCORPORATION AND POLYMER PROPERTIES

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The commercial importance of polyethylene (PE) is undeniable because it is the most widely produced polymer worldwide in terms of volume. Linear low-density PE which is one of the commercially available PE is a copolymer of ethylene and  $\alpha$ -olefins with density ranging between 0.91 – 0.94 g/cm³. The polymerization of ethylene in gas phase reactors is highly exothermic and hence, attention should be paid on how the heat should be removed. The removal of heat can often be achieved by adding chemically inert alkanes (C2-C6) often known as induced condensing agents (ICA), in either vapor or liquid form. These ICAs can serve as cosolvent to lighter components (ethylene) and anti-solvent to heavier component (1-hexene) a phenomenon called *cosolubility effect*. The presence of these ICAs have pronounced effect on the polymerization rate as well as final polymer properties.

In this study, gas phase copolymerization of ethylene with either 1-butene or 1-hexene in the presence of ethane, propane, and n-pentane as ICA was conducted. It was observed that when ethane is present up to 15 bars in the reactor, no impact on the observe rate of homopolymerization, molecular weight and crystallinity of ethylene-1-butene copolymers. For the copolymerization reaction, the initial rates actually decrease as the partial pressure of ethane increases. The reason for this observation is not clear as this was unexpected. Mass transfer resistance would be a possible explanation for this. It is possible that very high concentrations of inert components in the gas phase might actually obstruct the incoming of slowly reacting components to the interior of the particles. Hence, it is not impossible that higher pressure of ethylene caused the transfer of butene to be much slower than in the case of less dilute systems. At short times, it was observed that initial rates for 10 and 15 bars of ethane are almost similar to the homopolymerization rate. It is therefore concluded that ethane seems to have no observable influence on solubility of ethylene. The effect of ethane on the final polymer properties was also studied. The copolymer was slightly more crystalline at 15 bars of ethane, indicating that probably ethane acts as a weak antisolvent for butene. Nonetheless, if this is the case, the effect is very small and it is not likely that this high level of ethane is used in commercial PE processes

When propane is used as inert specie, the effect is more pronounced as compared to ethane. The impact of propane has positive cosolubility effect on ethylene with the polymerization rate. As the level of propane is increased up to 15 bars, the rate of polymerization also increases for both 1-butene and 1-hexene with this effect more noticeable in the presence of 1-hexene. This impact is also noticeable with respect to the MFI. As the level of propane increases, the MFI decreases (i.e the molecular weight increases) as the propane pressure increases. Contrariwise, the crystallinity of the copolymer clearly increases as the propane level increases. The explanation to this observation can be attributed to the fact that when propane level (cosolvent to ethylene) is increased, the concentration of ethylene in the amorphous phase of the polymer increases and consequently decreased the concentration of either comonomer in the polymer (propane act as antisolvent to either 1-butene or 1-hexene).

Finally, the effect is more pronounced when n-pentane is used as ICA. The variations in rate of polymerization as well as the final polymer properties (molecular weight and crystallinity) follow similar trends for the same explanation as that of propane. The result obtained when the copolymer samples are characterized using crystallization elution temperature shows that the presence of either propane or pentane, alters the comonomer incorporation by reducing the CH3/1000C with respect to similar copolymerizations performed without propane or pentane due to competing cosolubility effects.

#### Investigations of Mixing Behavior of Polymerization Processes

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In reaction engineering, a precise characterization of the applied reactor is crucial. In polymerization processes, the conversion and the microstructure of polymers are strongly influenced by temperature and concentration gradients.^[1] These gradients directly lead to the challenge of dead spaces, shortcircuiting and long-tailing of the reactor's mixing behavior.^[1] Reactor type and geometry as well as reaction mixture's viscosity strongly influence those back-mixing characteristics.^[2] To reveal and even avoid non-ideal mixing, investigations of the hydrodynamic behavior have to be performed within a specific reactor set-up.^[1] These considerations can be implemented in various ways. In principle, the mixing behavior can be directly analyzed in mini plants under lab conditions. However, this presents a complex and expensive alternative. An additional possibility is to set up models and conduct the respective simulations. Due to needed assumptions, the simulative outcomes can lead to uncertain results and have to be obligatorily validated by experiments. To investigate the hydrodynamic behavior of reactors in a simpler way, experimental model systems of reconstructed polymerization reactors can be used. Here, fluids come into operation which imitate the reaction mixture due to similar physical properties. This allows separate analysis of mixing to the actual polymerization mini plants. Advantageously, possible downtimes of the mini-plant and contaminating the set-up with impurities can be avoided.^[3]

This work concentrates on a measuring device for determining the back-mixing characteristics of polymerization reactors. The set-up is designed for a flexible change between different reactor geometries. Qualitative and quantitative aspects of mixing behavior are considered in measurements and the following evaluation. Two decisive factors are the residence time and the residence time distribution of the fluid inside the reactor examined in pulse experiments. By investigating the mixing times and the homogeneity of the reactor, the ideality of the mixing can be defined for various operating conditions. Via video recording of all measurements, the flow lines inside the transparent reactor are visualized and may be used for validating CFD simulations.

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#### Kinetic of Peroxide Decomposition considering the Impact of Solvent, Pressure and Peroxide Cocktail <u>Jana Sartorius</u>, Svenja Albus, Markus Busch*

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Peroxides possess a labile oxygen-oxygen bond which can split homolytically forming radicals induced by heat, pressure or radiation. Due to their decomposition, peroxides are applied as initiators for radical polymerisation. Therefore, their kinetic is a crucial part to understand and model these processes. Heating peroxides in a non-reactive solvent, their kinetic of decomposition can be investigated separately from polymerisation reactions.

LDPE is a broadly utilized polymer for numerous applications and produced using radical polymerisation on industrial scale. With pressure up to 3000 bar and temperature up to 300 °C, the handling and research of this process is a challenging task [1]. Due to the harsh conditions, reliable process near data is scarce. Buback [2] and Luft [3] investigated the kinetic of peroxide decomposition using IR measuring the increase of intensity correlating to a concentration increase of decomposition products. As a result of their temperature and pressure dependency, kinetic parameters such as activation energy, the reaction rate constant and activation volume can be evaluated. This optical setup is limited to low-viscous media showing transmission and can be handled in a flow cell. Therefore, the high-viscous conditions at the end of the polymerisation process are not accessible. Using high-pressure calorimetry for kinetic investigations this gap is tried to be filled.

The peroxide decomposition is highly exothermal causing intense heat flux and therefore calorimetric signals. The time-dependent enthalpy of decomposition contains its kinetic information which can be analysed by the Borchardt-Daniels method or thermokinetic software like THINKS [4]. The transitiometer enabling simultaneous control and recording of temperature, pressure and volume up to 3000 bar and 400°C is the mainly used device. Its isobaric mode allows investigations of pressure dependency and its pressuring system of solids and liquids including high-viscous media.

#### Influence factors

Former research focuses on the decomposition of peroxides in unpolar, low-viscous solutions of heptane or isododecane reflecting the chemical environment of ethylene. In consequence of the increasing viscosity during polymerisation progress and the variety of (co-)monomers, a broader range of physical properties should be represented by different solvents. Therefore, acetone, ethylbenzene, heptane, squalane and LDPE as matrix is investigated as solvent. An increase in viscosity limits the molecular freedom of movement leading to a higher energy demand for translation motion and therefore a higher decomposition temperature. Like the cage effect is caused by high viscosity, pressure can also change the mobility of molecules. The pressure effect on kinetic is expressed by the activation volume calculated from the pressure dependency of the reaction rate constant. The performed isobaric temperature scan between 100 bar and 2000 bar meets observation from Buback.

The chemical environment of peroxides can be influenced by the presence of another peroxide or its decomposition products. The use of peroxide cocktails is common for polymerisation starting the reaction smoothly, influencing the polymer properties and serving different stages of reaction but they are not investigated as a mixture in literature. In experiments a mixture of two peroxides decomposing at different temperatures shows a shift of kinetic parameters and decomposition temperature compared to the single peroxide.

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#### Analyses of polyacrylates using electrospray mass-spectrometry and

multi-angle-laser-light-scattering

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Homo- and copolymers of acrylates are used in a wide variety of applications, e.g., in adhesives, coatings, and biomedical materials. Despite the industrial importance of these polymer materials the complexity of the radical polymerization mechanism is still a topic of current research. The complexity of the mechanism is caused by a large number of elementary reactions that influence the overall polymerization rate and the topology of the polymers. For example, inter- and intramolecular transfer reactions associated with the formation of tertiary propagating radicals and subsequent  $\beta$ -scission of these mid-chain radicals at higher temperatures are still under investigation.

In this contribution polymerization reactions were carried out at high temperatures above 100°C up to 160°C which leads to the temperature-induced self-initiation of acrylic monomers. At high temperatures radical migration along the polymer backbone and the  $\beta$ -scission reaction become more important. Radicals can form branches with macromonomers from  $\beta$ -scission. Growth of tertiary radicals at the polymer-backbone also leads to branching.

Polymers produced at high reaction temperatures show characteristic low-molecular weight products as well as a high-molecular weight fraction. The low-molecular weight products are separated by fractionation using preparative SEC methods. The resulting samples were further concentrated for analysis in ESI-MS. The mass spectrometry results show  $\beta$ -scission products, as well as other elemental reactions such as transfer to the solvent in different intensities.

Unfractionated polymer samples are separated and analyzed using SEC-MALLS. Static laser-lightscattering at various scattering angles gives access to the absolute molecular weight and gyration radii of the polymers. With a linear and thus non-branched reference polymer, the branching ratio can be determined. These reference polymers cannot be produced by thermally initiated polymerizations at high temperatures, as side reactions quickly lead to branching points. Instead, photochemically initiated polymerizations at low temperatures are used. If the model of Zimm and Stockmeyer is applied, the average branching numbers per molecule are accessible. The number of branches in the polymer depends on the degree of polymerization. A strong dependence on the reaction temperature can also be observed. The data from the ESI-MS and the branching analysis are part of the experimental data set used for parametrization and validation of a kinetic Monte Carlo based model using the in-house developed simulator mcPolymer.

#### Implementation of an Inline-NIR-Spectroscopy to a High-Pressure System

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The free-radical polymerization of ethene to low-density polyethylene takes place at pressures between 1400 bar and 3500 bar and at temperatures between 130 C and 330 C.^[1] At those harsh conditions, it is challenging to get information out of the reaction system. Hence measurements are sometimes carried out offline, for example by taking a sample and analyzing it afterward. Inline measurements for in-situ analysis are favorable in terms of process control because of faster result times compared to offline methods.^[2]

In this work, a view cell with sapphire windows is introduced into the high-pressure system to make Fouriertransformation near-infrared (FT-NIR) spectroscopy possible. The near-infrared scope from 4500 cm⁻¹ to 10000 cm⁻¹ can be analyzed. The cell is suitable for applications up to 3000 bar and 300 °C. Requirements for the analysis are a homogeneous reaction medium and the intramolecular vibration of interest needs to change the molecular dipole moment. It is also necessary that a spectral line of interest does not overlap with another one for quantitative analysis.^[2,3]

In batch experiments, The half-band integrated intensity *B* of the first overtone of ethene was determined according to the integrated Lambert-Beer law. As expected from the literature, the half-band integrated intensity *B* is independent of temperature and pressure over a certain temperature and pressure range.^[4,5] During a continuous operation mode, spectra of the polymerization system were taken under steady-state conditions. The conversion of ethene is determined by the FT-NIR spectroscopy technique and is compared to the conversion determined gravimetrically by taking a polymer sample. The isosbestic point during polymerization meets the expectation of the literature.^[6]

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#### Kinetic investigation of the Dushman reaction for micromixing time calculation

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Mixing in industrial processes can improve the yield, selectivity and quality of the final product. While macromixing can be examined by dye or conductivity experiments, the investigation of micromixing processes needs chemical test reactions acting as a molecular probe. The Villermaux-Dushman reaction, which is a parallel competing reaction between an acid–base and the iodide iodate reaction yielding into iodine, is widely applied for micromixing experiments in various types of reactors. For micromixing time calculation, a detail knowledge of the underlying kinetic is needed. The kinetics of the Dushman reaction, especially the influence of the ionic strength on reaction rate constant, has been under frequent discussion. The most recent kinetic study conducted by Guichardon and Falk was performed with sulphuric acid and potassium sulphate [1]. At low concentration, sulphuric acid cannot be regarded as fully dissociated and potassium sulphate can act as a weak buffer which might have altered their kinetic investigation.

In this work, a kinetic investigation of the Dushman reaction was performed with perchloric acid and sodium perchlorate. To obtain accurate reaction rate constants for each investigated ionic strength, experimental data was fitted with the theoretical one with the reaction rate constant as the fitting parameter to obtain a minimal residual sum of squares. While the classical fifth-order rate law could be confirmed with a partial reaction order of  $IO_3^-1$ ,  $I^-2$  and  $H^+2$ , the reaction rate constant showed a difference by an order of magnitude. With the newly obtained reaction rate equation, accurate micromixing times calculations can be conducted.

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The design of pressure relief systems, such as those used in the high-pressure polymerization process, is usually done using regulations based on single-phase flows, such as API 520 [1]. In this context, the mass flow discharged in the event of relief is of central importance, since it determines the required relief cross-section. This mass outflow is essentially affected by the density of the ventilated medium as well as the valve characteristics. The required relief cross-section varies depending on the flow present. For example, the assumption of a single-phase flow leads to relief cross-sections that are too small when a two-phase system is relieved. Accordingly, an understanding of the relief characteristics of two-phase flows and consideration of the changing properties is essential for the design of safety devices.

A 34 mL view cell is used to visually analyze the relief from the high-pressure region. The image acquisition is done with a high-speed camera to show the occurring phenomena in detail. In addition, the temperature and pressure changes can be recorded via a fast measurement sensor system. For a more detailed investigation of the outflow characteristics of two-phase flows, various test parameters can be varied, such as the process conditions, the relief position and the nozzle length. The discharge takes place at a pressure of 2000 bar and different initial temperatures. Vinyl acetate is used as the comonomer, with the proportion being varied. The relief process itself is realized by a pneumatic diaphragm valve. High-pressure lines are used as the nozzle, the inner diameter and length of which can be varied so that the relief speed can be influenced.

An isentropic nozzle model according to J. Schmidt [2] is used to determine the relief velocity considering the different conditions and varied parameters. The model can be applied up to the point where phase separation occurs during expansion since the expansion process follows an isentropic behavior up to this point. In the further course, a two-phase flow must be assumed, whereby further factors must be considered. This is realized by the HNE-DS model of J. Schmidt [3]. The characterization of the boiling delay factor included in the calculation is enabled by the visualization of the relief process. This research intends to be able to simulate the relief process for single-phase as well as for two-phase flows, based on the isentropic nozzle model[2] as well as the HNE-DS model [3], to improve the design of safety devices.

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