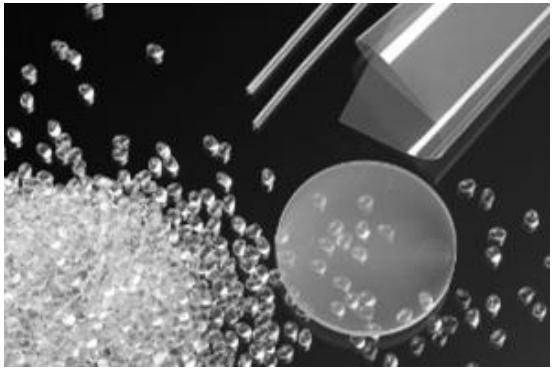
Conference Guide

4th PhD-Workshop on Polymer Reaction Engineering

30th October to 1st November 2015 in Fürstenfeldbruck



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Welcome to the 4rd PhD-Student Workshop on Polymer Reaction Engineering

Dear company representatives, professors and PhD-students,

The PhD-Student Workshop on Polymer Reaction Engineering represents an international platform where young researchers in the field of polymer reaction engineering can build up valuable networks. It is an opportunity to meet fellow PhD-students and to get into contact with interesting companies and potential employers. 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 forth time now and we would like to perpetuate it as an annual event. It has been launched in Lyon in 2012 with a total number of 35 participants. The second workshop has been organized in Hamburg in 2013 and involved 43 people. Last year it took place it San Sebastian with 37 attendees. This year we are recording a number 38 of registrations from universities as well as the industry.

Having participants from seven countries and various research fields we can look forward to an interesting and diverse workshop which contributions deal include the following topics:

- bulk, emulsion, miniemulsion, gas phase and high pressure polymerization
- structure-property relations regarding heat transfer, wettability and coagulation phenomena and extrusion as well as adhesion behavior
- homopolymers, copolymers, blends, foams, nanogels and hybridpolymers
- results obtained by new analytical methods

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

The Organizing Committee

Organizing Committee

Markus Busch	Chair of WPPRE, TU Darmstadt
Werner Pauer	Secretary of WPPRE, University Hamburg
Claudia Rost	TU Darmstadt
Baldur Schröter	University Hamburg
Kristina Zentel	TU Darmstadt

Sponsors

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

Transfer from the Airport into Munich

From the airport you either take the train number S1 or S8 to the main station of munich. This takes approximately 45 minutes.
From the main station you can get to the old city center by foot (ca. 15 min walk) or by taking a train (S1,2,3,4,6,7 or 8) from the main station to the stop Marienplatz.

Transfer from Munich to Fürstenfeldbruck

To get to Fürstenfeldbruck from the main station in Munich you can take train S4 in the direction of Grafrath. The train takes 26 mins for this route and runs approximately every 20 mins.
From the train station in Fürstenfeldbruck (1) it takes about 10 mins to walk to the Hotel Fürstelfelder (2). From there it takes another 10 mins to get to the Veranstaltungsforum (Event Forum) Fürstenfeld (3), where the workshop is going to take place.

Hotel and Event Forum Adress

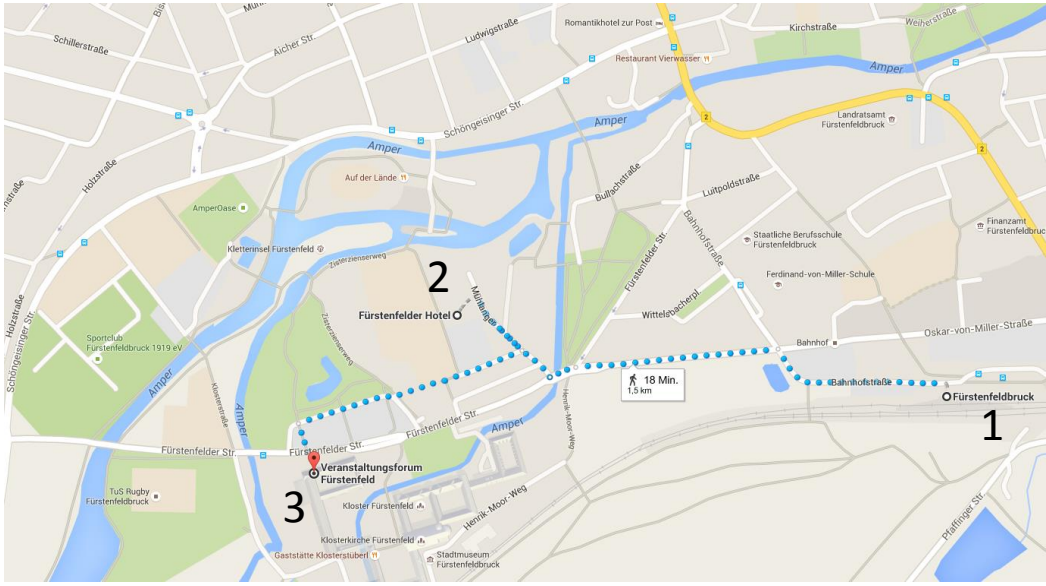
Hotel Fürstenfelder
Mühlanger 5
82256 Fürstenfeldbruck
(+49) 8141 888 750

Veranstaltungsforum Fürstenfeld
Fürstenfeld 12
82256 Fürstenfeldbruck
(+49) 8141 666 51 40

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://www.efce.info/PhD_Workshop+of+WPPRE.de



General Information

Language

The official language at the workshop is English.

Internet

You will be provided access to the WLAN in the Veranstaltungsforum Fürstenfeld when registering on Friday.

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

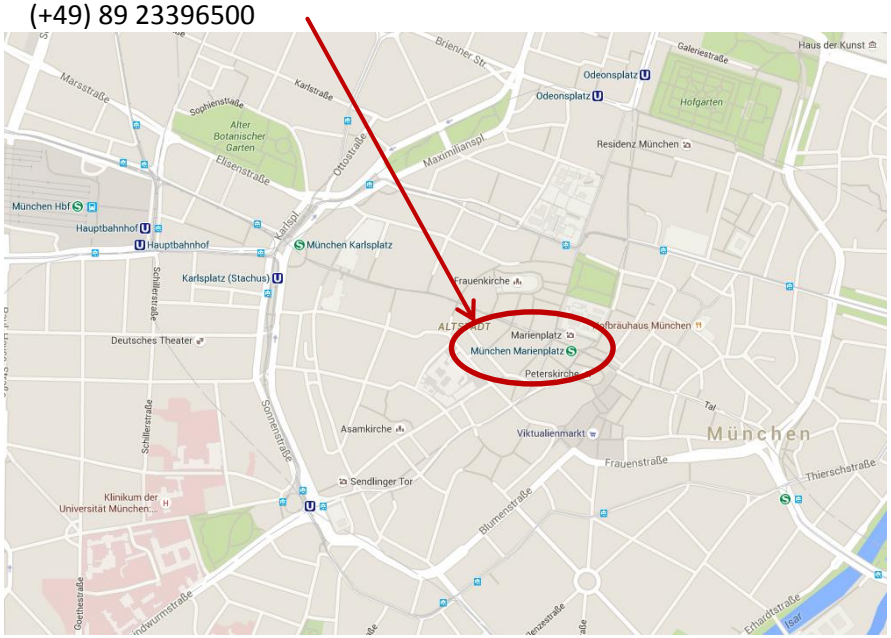
Police	110
Firebrigade	112
Ambulance	112

Taxi numbers

(+49) 8141 14 28
(+49) 8141 19 410
(+49) 8141 33 666

Tourist information

Marienplatz, 8 (old town)
(+49) 89 23396500



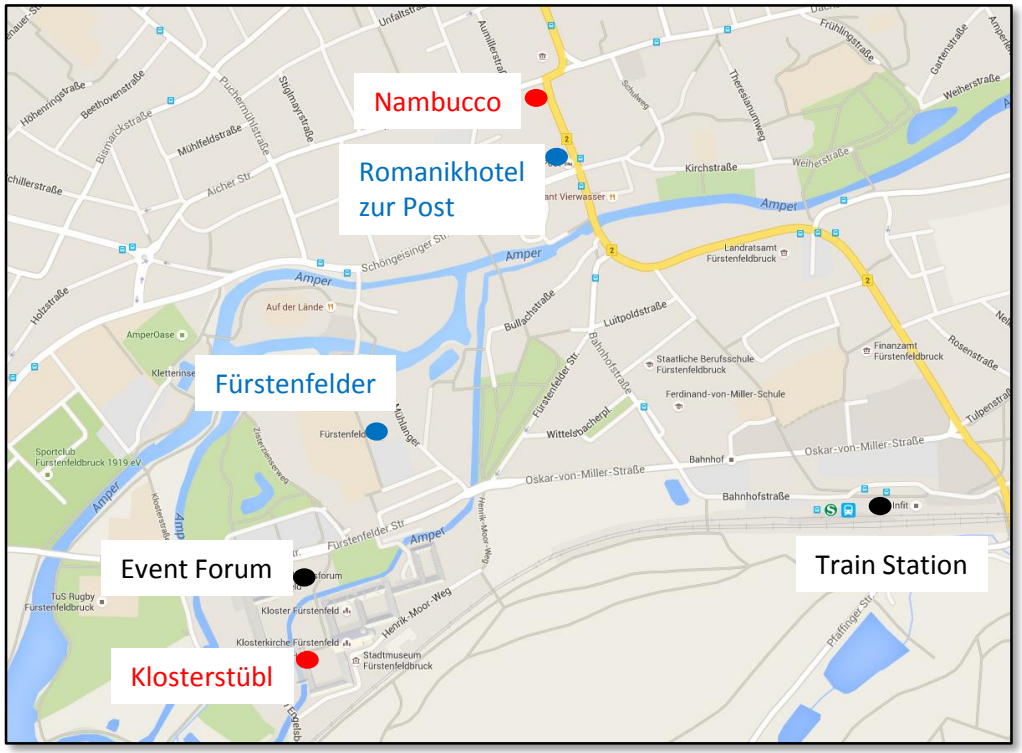
Places to know

TECHNISCHE UNIVERSITÄT DARMSTADT

Veranstaltungsforum Fürstenfeld

Fürstenfeldbruck Overview

- Hotels
- Restaurants
- Event Forum



Programme by Days

Friday, 30th October 2015

TECHNISCHE UNIVERSITÄT DARMSTADT

15:00 -16:30 **Registration at the conference site**
Poster wall preparation

16:30 -16:45 **Welcome**
Prof. Markus Busch

Session I: Polymerization Techniques

Chair: Kristina Zentel (Technical University Darmstadt)

16:45 -17:05 **Jan Georg Rosenboom** (ETH Zürich)
Ring-Opening Polymerization (ROP) for High Molecular Weight Polyethylene Furanoate (PEF) Synthesis and the Analysis thereof using Diffusion NMR (DOSY)

17:05 -17:25 **Ehsan Meharvar** (Polymat)
Comb-Like Acrylic-Based Polymer Latexes Containing Nano-Sized Crystalline Domains

17:25 -17:45 **Sergej Diez** (University Hamburg)
Characterization of Sulfur Copolymers prepared by Inverse Vulcanization

17:45 -18:05 **Joana Kettner** (Martin-Luther-University, Halle)
Kinetic Study of the Bulk Polymerization of Propylene with a Metallocene Catalyst using Reaction Calorimetry

18:05 -18:25 **Alicia De San Luis** (Polymat)
Nanostructured Polymeric Aqueous Dispersions containing Quantum Dots

18:25 -19:00 **Coffee Break and Poster Session**

19:00 -19:30 **Dr. Ursula Tracht (LANXESS)**
LANXESS Performance Polymers: Products, Careers & Assignments

20:00 **Dinner at Klosterstüberl**
Fürstenfeld 7C, Fürstenfeldbruck

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Programme by Days

Saturday, 31st October 2015

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Session II: Modelling

Chair: Andra Nistor (University of Chemistry & Technology Prague)

08:50 - 09:10 **David Eckes** (Technical University Darmstadt)
Theoretical Evaluation of the Mechanical Degradation within an Industrial Multi-Zone LDPE Autoclave Reactor

09:10 - 09:30 **Esther Laryea** (Karlsruher Institute of Technology)
The Influence of Fluid Dynamics on the Kinetics of Free-Radical Polymerization

09:30 - 09:50 **Kristina Zentel** (Technical University Darmstadt)
Impact of Thermo-Physical Data on the Modelling of High Pressure Polymerizations

09:50 - 10:10 **Baldur Schroeter** (University Hamburg)
Spectroscopic Investigations on a Redox Initiator System for continuous Emulsion Polymerization

10:10 - 10:30 **Peter Fleckenstein** (ETH Zürich)
Modelling of the Ring Chain Equilibrium in Cyclic Oligomers of Polyethylene Furanoate (PEF)

10:30 - 11:10 **Coffee Break and Poster Session**

Session III: Emulsion Polymerization

Chair: Baldur Schroeter (University Hamburg)

11:10 - 11:30 **Kristina Rossow** (University Hamburg)
Tubular Reactor Concept for Process Intensification in Emulsion Polymerization

11:30 - 11:30 **Barthélémy Brunier** (LAGEP / CNRS-University of Lyon)
Analysis of the effect of Laponite® on Radical Exchange in Seeded Semibatch Pickering Emulsion Polymerization

Programme by Days

Saturday, 31st October 2015

11:50 - 12:10 **Sevilay Bilgin** (Polymat, University of the Basque Country)
Synthesis and Characterization of Emulsifier-Free High Solids Content Waterborne Polymers

12:10 - 12:30 **Olessya Loiko** (Eindhoven University of Technology)
New Synthetic Route Towards Anisotropic Polymer-Gibbsite Latex Particles

12:30 - 13:00 **Dr. Wolfgang Gerlinger (BASF)**
Polymer Reaction Engineering at BASF

13:00 - 14:00 **Lunch**
Veranstaltungsforum Fürstenfeld

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Session IV: Process Design and Improvement

Chair: Ehsan Meharvar (Polymat)

14:00 - 14:20 **Marzieh Riahinezhad** (University of Waterloo)
How to Go Full Circle from Polymerization Kinetics (Fundamentals) to Final Desirable Application Properties (Applied Engineering)?

14:20 - 14:40 **Ladislav Konopka** (University of Chemistry&Technology Prague)
Triboelectric Charging of Polyethylene

14:40 - 15:00 **Thomas Höchfurtner** (Johannes Keppler University, Linz)
Kinetics of a Multi-Stage Polymerization of Olefins in a Single-Reactor Setup

15:00 - 15:20 **Gunnar Spiegel** (Johannes Keppler University, Linz)
Experimental Investigation of Z-N Catalyst Pre-Contacting on Polymerization

15:20 - 15:40 **Muhammad A. Bashier** (CNRS-University of Lyon)
The Effect of Silica Dehydroxylation Temperature on Catalytic Performance of Supported (n-BuCp)$_2$ZrCl$_2$ in Ethylene Polymerization

Programme by Days

Saturday, 31st October 2015

15:40 - 16:30 **Coffee Break and Poster Session**

16:30 - 17:00 **Diego Castañeda-Zúñiga (SABIC)**
Technology and Innovation at SABIC

Session V: Thermodynamics

Chair: Barthélémy Brunier (LAGEP / CNRS-University of Lyon)

17:00 - 17:20 **Eric Fischer** (ETH Zürich)
A Novel Approach to Determine Partition Coefficients of Monomers in Polymer Dispersions via Headspace Gas Chromatography

17:20 - 17:40 **Andra Nistor** (University of Chemistry & Technology Prague)
Open- and Closed-Cell Polystyrene Foams Prepared by Thermally Induced Phase Separation

17:40 - 18:00 **Martina Podivinská** (University of Chemistry & Technology Prague)
Thermodynamics of Sorption and Swelling in Polyethylene under Gas- and Liquid-Phase Polymerization Conditions

18:00 - 18:20 **Mario Quade** (University Hamburg)
Process Design for Sulfuric Acid Leaching of Iron Bearing Slags

15:40 - 16:30 **Coffee Break and Poster Session**

19:30 **Dinner at Nambucco**
Hauptstraße 25, Fürstenfeldbruck

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Programme by Days

Sunday, 1st November 2015

10:30 **Guided tour through the historic center of Munich**

Meeting point: Odeonsplatz in the historic center

Tour kindly sponsored by

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12:00 **Lunch in the Ratskeller**

Marienplatz 8, Munich

Lunch kindly sponsored by

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

Ratskeller, Marienplatz 8, Munich

The prize for the best poster contribution is kindly sponsored by

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List of Posters

1. **B. Brunier, Y. Chevalier, N. Sheibat-Othman**
   Analysis of the Effect of Laponite® on Radical Exchange in Seeded Semibatch Pickering Emulsion Polymerization

2. **G. Spiegel, P. Aigner, C. Paulik**
   Experimental Investigation of Z-N Catalyst Pre-contacting on Polymerization

3. **T. Hellwig, W. Pauer, H.-U. Moritz**
   Investigation of the Redox-Initiated Polymerization in Levitated Single Droplets

4. **O. Loiko, B. Spoelstra, A.M. van Herk, J. Meuldijk, J.P.A. Heuts**
   New Synthetic Route Towards Anisotropic Polymer-Gibbsite Latex Particles

5. **S. Bilgin, R. Tomovska, J. M. Asua**
   Synthesis and Characterization of Emulsifier-Free High Solids Content Waterborne Polymers

6. **A. De San Luis, A. Bonnefond, S. Marre, C. Aymonier, M. Paulis, J. R. Leiza**
   Nanostructured Polymeric Aqueous Dispersions Containing Quantum Dots

7. **A. Nistor, M. Toulec, A. Zubov, J. Kosek**
   Polymer Foams with Improved Heat Insulation Properties

8. **L. Konopka, S. Jantač, J. Kosek**
   Triboelectric Charging of Polyethylene

9. **S. Griebenow, M. Busch**
   Modelling of Technical Reactors for the Production of Ethylene Copolymers

10. **D. Eckes, A. Hilfer, M. Busch**
    Theoretical Evaluation of the Mechanical Degradation within an Industrial Multi-Zone LDPE Autoclave Reactor

11. **M. Balyschewa, M. Busch**
    Application of Zirconocendichlorid in the Ethylene Polymerization under High Pressure Conditions

12. **J. Kettner, M. Bartke**
    Kinetic Study of the Bulk Polymerization of Propylene with Metallocene Catalyst using Reaction Calorimetry

13. **K. Rossow, W. Pauer, H.-U. Moritz**
    Tubular Reactor Concept for Process Intensification in Emulsion Polymerization

List of Posters

14. **M. Quade, W. Pauer, A. Heidel, H. Kadereit, H.-U. Moritz**
Process Design for Sulfuric Acid Leaching of Iron Bearing Slags

15. **J.-G. Rosenboom, G. Storti, M. Morbidelli**
Ring-Opening Polymerization (ROP) for High Molecular Weight Polyethylene Furanoate (PEF) Synthesis and the Analysis thereof Using Diffusion NMR (DOSY)

16. **E. Fischer, G. Storti, M. Morbidelli**
A Novel Approach to Determine Partition Coefficients of Monomers in Polymer Dispersions via Headspace Gas Chromatography

17. **P. Fleckenstein, G. Storti and M. Morbidelli**
Modeling of the Ring Chain Equilibrium in Cyclic Oligomers of Polyethylene Furanoate (PEF)

List of Participants

	Name	Institution
1.	Bashir, Muhammad Ahsan	LAGEP / CNRS-University of Lyon
2.	Balyschewa, Margarita	Technical University Darmstadt
3.	Busch, Markus Prof. Dr.	Technical University Darmstadt
4.	Bilgin, Sevilay	Polymat
5.	Brunier, Barthélémy	LAGEP / CNRS-University of Lyon
6.	Castañeda-Zúñiga, Diego Mauricio	SABIC
7.	De San Luis, Alicia	Polymat, Centro Joxe Mari Korta
8.	Diez, Sergej	University Hamburg
9.	Eckes, David	Technical University Darmstadt
10.	Fischer, Eric	ETH Zürich
11.	Fleckenstein, Peter	ETH Zürich
12.	Gerlinger, Wolfgang Dr.	BASF
13.	Griebenow, Sascha	Technical University Darmstadt

List of Participants

	Name	Institution
14.	Grolman, Eric Dr.	DSM
15.	Hellwig, Thomas	University Hamburg
16.	Höchfurtner, Thomas	Johannes Keppler University Linz
17.	Kettner, Joana	Martin-Luther University Halle-Wittenberg
18.	Konopka, Ladislav	University of Chemistry and Technology Prague
19.	Kosek, Juraj Prof. Dr.	University of Chemistry and Technology Prague
20.	Kröner, Thomas Dr.	Novolen Technology
21.	Laryea, Esther	Karlsruher Institute of Technology
22.	Loiko, Olessya	Eindhoven University of Technology
23.	Mehravar, Ehsan	Polymat
24.	Nistor, Andra	University of Chemistry and Technology Prague
25.	Othmann, Nida Dr.	University of Lyon
26.	Paulik, Christian Prof. Dr.	Johannes Keppler University Linz

List of Participants

	Name	Institution
27.	Podivinská, Martina	University of Chemistry and Technology Prague
28.	Quade, Mario	University of Hamburg
29.	Riahinezhad, Marzieh	University of Waterloo
30.	Rosenboom, Jan-Georg	ETH Zürich
31.	Rossow, Kristina	University Hamburg
32.	Rost, Claudia	Technical University Darmstadt
33.	Schroeter, Baldur	University of Hamburg
34.	Schulze, Uwe Dr.	Synthomer
35.	Spiegel, Gunnar	Johannes Keppler University Linz
36.	Spiegel, Stefan Dr.	Wiley VCH, Macromolecular Journals
37.	Tracht, Ursula Dr.	LANXESS
38.	Zentel, Kristina	Technical University Darmstadt

Book of Abstracts

TECHNISCHE UNIVERSITÄT DARMSTADT

1. Jan Georg Rosenboom
2. Ehsan Meharvar
3. Sergej Diez
4. Joana Kettner
5. Alicia De San Luis
6. David Eckes
7. Esther Laryea
8. Kristina Zentel
9. Baldur Schroeter
10. Peter Fleckenstein
11. Kristina Rossow
12. Barthélémy Brunier
13. Sevilay Bilgin
15. Olessya Loiko
16. Marzieh Riahinezhad
17. Ladislav Konopka
18. Thomas Höchfurtner
19. Gunnar Spiegel
20. Muhammad A. Bashier
21. Eric Fischer
22. Andra Nistor
23. Martina Podivinská
24. Mario Quade
25. Margarita Balyschewa
26. Sascha Griebennow
27. Thomas Hellwig

Ring-opening polymerization (ROP) for high molecular weight polyethylene furanoate (PEF) synthesis and the analysis thereof using diffusion NMR (DOSY)

J.-G. Rosenboom, Giuseppe Storti, Massimo Morbidelli
ETH Zurich, Institute for Chemical and Bioengineering, Vladimir-Prelog-Weg 1, 8093 Zurich, Switzerland

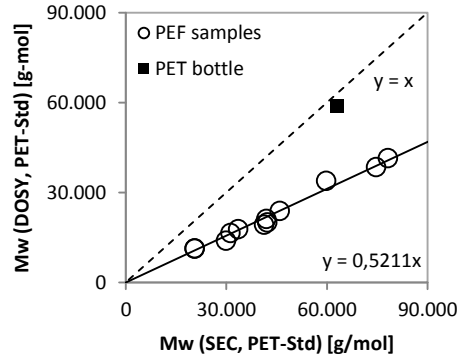
Along the shift of our societies from fossil-fuel based economies towards more sustainable civilizations, ring-opening polymerization (ROP) can be an alternative process to synthesize a novel class of renewable resource-based polymers. Furanic polyesters like polyethylene furanoate (PEF) have been ranked among the top potential chemicals by the US-DOE and may replace one of the world's dominant fossil-based plastics, polyethylene terephthalate (PET). Those alternative polymers have already been investigated and produced solely via polycondensation (PC) by a few research groups and companies such as Avantium incentivized by Coca-Cola [1-3]. ROP proceeds via living chain-growth mechanisms and thus may offer the advantages of better MW control, shorter reaction times and obsolete condensation product removal. As an alternative and facile method to measure MW of PEF we present diffusion NMR (DOSY) [4].

High molecular weight PEF via ROP. We produce high molecular weight (MW) PEF with a competitive process based on ring-opening polymerization (ROP). In contrast to PC, our ROP-based PEF synthesis does not require byproduct removal and thus reaction can be completed with conversions >95% after several minutes rather than days. Those fast reactions were performed in bulk at elevated temperatures above 270°C, which were high enough to melt or plasticize the cyclic monomers. Degradation of polymer and catalyst may occur after 15-30 minutes. However, reaction in solution at lower temperatures around 180°C have proven very slow and resulted in limited molecular weights. High molecular weights surpassing the requirements for plastic bottle blowing (60'000 g/mol, by SEC) have been produced in melt using several tin- and metal oxide catalysts. The coloring of PEF products, already reported in the literature, was found dependent on cyclic monomer purity and catalyst use. Lower reactivity or susceptibility to catalytic conversion could be assessed to the dimeric monomer species, while higher species were readily reacted. Maximum achievable molecular weight increased with general monomer purity. The higher glass temperature and lower melting point compared with PET allow for higher thermal stability and easier processing of the final bottles, respectively.

Molecular weight analysis with NMR DOSY.

While PEF is a polymer with promising characteristics, it challenges established MW analysis methods such as size exclusion chromatography (SEC), as it is only soluble in expensive solvents such as hexafluoro-2-propanol (HFIP) and requires special HFIP-resistant equipment.

In order to establish NMR DOSY as a facile method, we investigated the relevant parameters influencing diffusion and the NMR measurement itself. NMR DOSY applies pulsed field gradients to spatially label molecules and thus track their diffusive motion via size-dependent signal loss after magnetization refocussing. Using double stimulated echo pulse (dstegpd2) sequences for convection correction (CC) allowed very robust conduct of experiment in contrast to using simpler single stimulated echo sequences without CC. Sample concentration should be around 0.4 ± 0.1 mg/mL to balance the trade-off between good signal-to-noise and influence of concentration on viscosity and molecular crowding. A calibration using PET standards is readily established. A comparison of DOSY vs SEC results shows a clear linearity, while the observed offset of 50% underlines the different coiling behaviour of PEF in the applicable solvents. Molecular dynamics simulations on this topic are ongoing. NMR DOSY can compete with SEC on solvent use and measurement time. While adjusting diffusion times Δ to achieve full signal attenuation along the gradient strength curve is usually recommended, using a fixed average Δ for all standards and samples can save measurement time without significant loss of precision.



REFERENCES

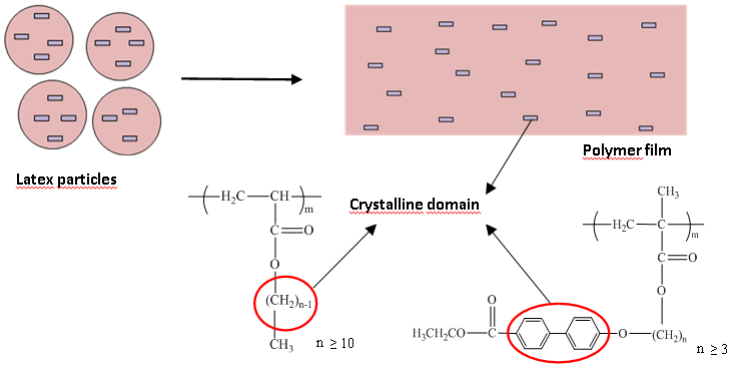
[1] M Gomes, A Gandini, A J D Silvestre, B Reis. J. Polym. Sci., Part A: Polym. Chem., 49, 3759–3768, **2011**.
[2] Thiyagarajan S et al, and van Haveren J, van Es DS. Green Chem., 16, 1957-1966, **2014**.
[3] L Sipos, E De Jong, M A Dam, J M Gruter. In: P Smith et al., ACS Symposium Series, 1105, 1-11, **2012**.
[4] Li W, Chung H, Daeffler C, Johnson JA, Grubbs RH, Macromolecules, 45, 9595-9603, **2012**.

Comb-Like Acrylic-Based Polymer Latexes Containing Nano-Sized Crystalline Domains

E. Mehravar, J. R. Leiza, and J. M. Asua
POLYMAT and Grupo de Ingeniería Química, Dpto. de Química Aplicada, University of the Basque Country UPV/EHU, Joxe Mari Korta Zentroa, Tolosa Etorbidea 72, 20018, Donostia/San Sebastián, Spain
(*ehsan.mehravar@ehu.es*)

(Liquid) crystalline domains are known to impart improved mechanical properties for solvent born systems [1]. However, little is known about the synthesis of these domains and their properties in water borne acrylic-based latex particles [2]. These hard and tough domains can be introduced to a polymer matrix by: (1) using crystallisable side-chains of the polymer backbone obtained via copolymerization of monomers having long side chains with conventional monomers (comb-like crystalline polymers) [3] or (2) using polymer liquid crystals (PLC) formed by introducing rod- or disc-like mesogenic groups. Mesogenic monomers having side-chain PLCs seem to be more suitable for free radical polymerization (Figure 1).

In this work the mechanical properties of the soft acrylic-based latex particles via introducing crystallizable units or liquid crystalline domains within the waterborne latex particles was studied. The polymer latexes were synthesized via 2-step seeded miniemulsion copolymerization of a crystallizable long side chain acrylate monomer (stearyl acrylste, SA) (first method) or side chain liquid crystalline monomer (second method) and short side chain (meth)acrylates (methyl methacrylate MMA, n-buthyl acrylate BA and Acrylic acid AA) in different compositions. Thermal characterization of the films prepared from these latexes indicated that the heat of fusion and crystallinity of the copolymer latexes decrease with increasing short side chain (meth)acrylates concentration. The mechanical properties of the films showed that the presence of polymer liquid crystal domains and polystearyl acrylste(PSA) crystalline units increase the mechanical properties of the latexes. Conversely, the PSA amorphous states decrease the glass transition temperature and mechanical properties of the copolymer latexes.



References

[1] Chen, D. S.; Jones, F. N., Journal of applied polymer science , **1988**, 36, 141-163.
[2] Parker, H. Y.; Merritt, R. F.; Fu, Z.; Ibbitson, S. A.; Gore, R. H.; Wolfersberger, M. A., U. S. Patent 6,552,147, **2002**.
[3] O'Leary, K.; Paul, D. R., Polymer , **2006**, 47, 1245-1258.

Your notes:

Characterization of Sulfur Copolymers prepared by Inverse Vulcanization

Sergej Diez, H.-U. Moritz, P. Theato, W. Pauer*, A. Florian, Institute for Technical and Macromolecular Chemistry, University of Hamburg, Hamburg/Germany*

Email: theato@chemie.uni-hamburg.de or pauer@chemie.uni-hamburg.de

The interest in utilizing elemental sulfur as a feedstock for novel polymeric materials has recently developed. The group of PYUN established a synthetic protocol, named inverse vulcanization, to prepare numerous polymeric structures derived from sulfur and vinylic comonomers.[ ] While these copolymer materials found application as cathode materials in Li-S batteries, [, ,] their mechanical and electrical properties are virtually unexplored.[ ]

Hence, in the present study we synthesized amorphous, hydrophobic and translucent polymeric sulfur networks, which provide a high thermal resistance. The polymeric material properties of the novel sulfur copolymers can be controlled by variation of monomers as well as the feed ratio. Two comonomers, divinylbenzene (DVB) and 1,3-diisopropenylbenzene (DIB), have been investigated. The properties of the obtained materials range from plastic to elastic and thermosets to melting pastes (waxy or doughy), respectively. Results of the mechanical characterization, like stress-strain experiments and dynamic mechanical thermal analysis, are discussed and support the polymeric cross-linked network structure. We are convinced that this variability of sulfur copolymers will lead to alternative applications.

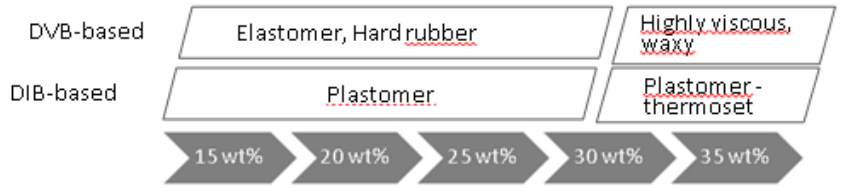


Figure 1. Dependence between polymer type and monomer ratio.

REFERENCES

[1] J.Pyun et al., *The use of elemental sulfur as an alternative feedstock for polymeric materials*, Nature Chem., **2013**, 5, 518–524.

[2] J.Pyun et al., *Inverse vulcanisation of elemental sulfur to prepare polymeric electrode materials for Li S Batteries*, ACS Macro Lett. **2014**, 3, 229−232; J. Pyun, et al., *Kilogram scale inverse vulcani-zation of elemental sulfur to prepare high capacity polymer electrodes for Li-S batteries*, J.Polym. Sci., **2015**, 53, 173-177.

[3] E. T. Kim et al., *One-pot synthesis of PbS NP/sulfur-oleylamine copolymer nanocomposites via the copolymerization of elemental sulfur with oleylamine*, Polym. Chem., **2014**, 5, 3617-3623.

[4] B. Duan et al., *Carbyne polysulfide as a novel cathode material for lithium/sulfur batteries*, J. Mater. Chem. A, **2013**, 1, 13261–13267.

[5] J. Pyun et al., *preparation of dynamic covalent polymers via inverse vulcanization of elemental sulfur*, ACS Macro. Lett., **2014**, 3, 1258-1261.

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Your notes:

Kinetic study of the bulk polymerization of propylene with metallocene catalyst using reaction calorimetry

J. Kettner, M. Bartke,
Martin-Luther University Halle-Wittenberg, Polymer Reaction Engineering, Heinrich-Damerow-Str. 4, 06120 Halle, Germany
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Purpose of the presented study is the kinetic investigation of the bulk polymerization of propylene with a supported metallocene catalyst. The experiments were carried out using a reaction calorimeter from ChemiSens® which is based on the principle of heat flow calorimetry [1], [2], [3].

The main advantage of the calorimeter is that heat generated from the polymerization reaction is measured independent of heat transfer conditions and filling level of the reactor. Therefore, no calibration is needed. The heat flow is measured via heat conductivity in the reactor base. The heat input of the stirrer is recorded by means of a torque transducer. The reaction kinetics can be directly determined from the generated chemical heat of the reaction, because it is direct proportional to the reaction rate.

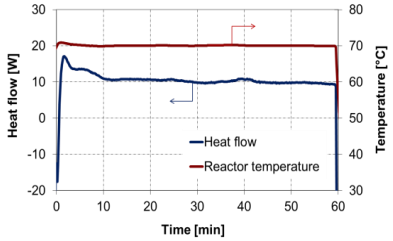

Fig.1: Measured heat flow during polymerization reaction

$\rightarrow \dot{Q}_{chem} = V_R \cdot R_P \cdot (-\Delta_R H) = \dot{Q}_{Heat\ flow} - P_{Stirr}$

In this study polymerizations were carried out using a prepolymerized catalyst which was injected into the reactor directly under reaction conditions. The influence of different reaction temperatures and hydrogen concentrations on the catalyst activity was investigated

Based on the experimental results a simplified kinetic model was developed describing the kinetics of the bulk polymerization of propylene with metallocene catalyst. The modelling and simulation were carried out using the software gPROMS ModelBuilder (Process Systems Enterprise). With the derived model the kinetic parameters of the catalyst were estimated and activity profiles of the reaction were calculated. Average molecular weights were determined using the method of moments.

[1] Samson, Weickert et al.: AlChe journal 44 (1998), p. 1424-1437
[2] Korber et al.: Macromol. Chem. Phys. 202 (2001), p. 3329-3333
[3] Pater et al.: Chem. Eng. Sci. 57 (2002), p. 3461-3477

Your notes:

Nanostructured polymeric aqueous dispersions containing quantum dots

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Quantum dots are semiconductor nanocrystals ranging in size from 1 nm to 10 nm formed from periodic elements of groups II-VI, III-V and IV-VI (CdSe, InAs, PbSe). They exhibit interesting size-tunable electronic and optical properties, that allow them to be used in a wide range of applications such as in biology, for photovoltaic devices and light emitting devices [1,2]. In order to prevent the loose of luminescence because of possible defects in the core surface the nanocrystal is usually passivated with a semiconductor material, such as ZnS, leading to core-shell structures that are later modified with an organic compound (TOPO, ODA...) or an amphiphilic polymer.

Because of their heavy-metal structure many of these applications require the combination quantum dots/polymer creating organic-inorganic hybrid particles[2]. This polymer covering has two objectives, on the one hand the protection of the environment from the quantum dots toxicity, and on the other hand the protection of the quantum dots from photo degradation or damage caused upon mechanical manipulation.

The aim of this work is, on one hand, to encapsulate different types of quantum dots in polymer particles so they can be used as biosensors for multiplexing[2,3] and on the other hand the synthesis of a wide range of sizes of core and core/shell quantum dots modified on their surface with different molecules.Initially for the first purpose, 7 nm CdSe/ZnS quantum dots coated with octadecylamine as surface modifier have been used in batch[3,4] and semi-batch miniemulsion polymerization. The obtained hybrid organic-inorganic latexes have been characterized using transmission electron microscopy and fluorescence microscopy. For the second purpose quantum dots are synthesized in a continuous reactor under supercritical conditions using hexane as supercritical fluid [5]. Changing the conditions quantum dots of different sizes and shapes can be obtained, both for core and core/shell nanoparticles. The characterization is done using transmission electron microscopy and quantum yield measurements.

Different aspects of the experimental work and results will be discussed in the presentation

References

[1] Alivisatos, A.P, *Science, 271*, 933-937, **1996**
[2] Tomczak, N et al, *Progress in Polymer Science, 34*, 393-430, **2009**
[3] Joumaa, N et al , *Langmuir* , *22*, 1810-1816, **2006**
[4] Esteves, A.C et al, *J. Nanosci. Nanotechinology* , *5*, 766-771, **2005**
[5] Marre, S et al, *Adv. Mater* , *20*, 4830-4834**, 2008**

Your notes:

Theoretical Evaluation of the Mechanical Degradation within an Industrial Multi-Zone LDPE Autoclave Reactor

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Low Density Polyethylene (LDPE) is a mass product that is produced industrially in the amount of several million tons per year. It is hereby produced under high pressures (1300 - 3000 bar) and high temperatures (180 - 300 °C) via mass polymerization in a supercritical phase. Since the first commercial plant two different reactor types have been established: On the one hand the tubular reactor and on the other hand the continuously stirred autoclave reactor. Both reactor types produce LDPE grades that are highly specific with regards to their application. For example LDPE formed by an autoclave reactor is best suited for coating applications, due to the different topology of the macromolecules produced by this reactor type. In contrast to a tubular reactor, an autoclave reactor can produce polymer molecules that become very large and form a so-called high molecular tail or shoulder. The origin of this characteristic molecular weight distribution is of special interest and still widely discussed in literature.

Kim et. al.[1] formulated the so called scission paradox. They stated that the basic kinetic model of the ethylene polymerization is not able to describe a high molecular shoulder, when the branched structure of LDPE is taken into account. The reason is based on the assumption that fragmentation of polymer molecules only happens via β-scission. By now several explanations were proposed in order to describe the typical high molecular shoulder, reaching from mixing effects[2], to gelation[3], and the mechanical degradation of polymer molecules[4].

The work presented here focuses on the mechanical degradation of polymer molecules as the origin of the high molecular shoulder. We found that this approach is able to reproduce the high molecular part of the molecular weight distribution very accurately and consistently throughout stochastic and deterministic models. By applying the physical models of Hinch[5] we are able to describe a high molecular tailing as well as a shoulder. The mechanical degradation of large polymer molecules due to shear within the reactor is applied to different operating conditions of an industrial multi-zone autoclave reactor.

Additionally, fluid dynamic calculations are presented allowing access to the flow field and the forces acting on a polymer molecule. This detailed analysis allows assessing the possibility of mechanical degradation and localizing domains where it may happen within the industrial process.

REFERENCES

[1] Iedema, P. D.; Wulkow, M. Hoefsloot, H. C. J, *Macromolecules*, **2000**, *33*, 7173-7184
[2] Wells, G, Ray, W. H., Macromol. *Mat. and Eng.,* **2005**, *290*, 4.
[3] Yaghini, N, Iedema, P. D., *Macromolecules*, **2014**, *47*, 15.
[4] Kim, D.-M., Busch, M., Hoefsloot, H. C. J., Iedema, P. D*., Chem. Eng. Sci*., **2004**, *59*, 13.
[5] Hinch, E. J., *Phys. of Fluids*, **1977**, *20*, 22.

Your notes:

The Influence of Fluid Dynamics on the Kinetics of Free- Radical Polymerization

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Free-radical polymerization is one of the most important techniques used industrially for the synthesis of polymers. It is robust and allows a high variety of initiators, solvents and process conditions. The field of Polymer Reaction Engineering moves more and more in the focus of research and industry because of the expanding demand of tailor-made polymers- and the subsequent growth of the polymer industry. Polymer Reaction Engineering is the connection between Polymer Chemistry and Process Engineering and links up their knowledge. The central research on this field is focused on clarifying the effects of process types and characteristics on product properties and productivity. The development of new polymerization reactors, like a Spinning Disc Reactor, is also part of Polymer Reaction Engineering. In order to control, regulate and optimize or rather to develop new production processes, models and simulations of the polymerization processes are necessary. Thereby, the kinetics of the reaction is interrelated to the influence parameters of the process. The fluid dynamics inside of a reactor is one of the important determining factors on the macroscopic level, which comes to the fore with the raising diversity of reactors. The dependency between fluid dynamics and polymerization kinetics has already been registered in some manuscripts [1, 2]. However, there is no detailed investigation which neither gives information about the reason of the phenomena observed on a molecular level nor a quantitative description.

For this reason, the present work deals with the influence of the fluid dynamics on the reaction kinetics of free-radical polymerization. Thereby, all rate constants of the kinetics are determined as a function of characteristic numbers, which are used to describe the fluid dynamics. Therefore, laboratory experiments were performed in a Taylor-Couette reactor (TCR), which consists of two concentric cylinders. Considering the rotation of the inner cylinder the reaction takes place in the gap while the reaction mixture is sheared. The shear rate can be varied by a change of the gap width respectively by a change of the rotational speed. Methyl methacrylate (MMA) in xylole initiated by AIBN was used as a model system. The results show that both the monomer conversion and the molecular weight distribution are influenced by the shear rate. Additionally, a dependency of the reaction mixture composition and the influence of the shear rate was found. For the determination of the rate constants methods taken from literature are mostly used [3][4][5]. A comparison of the rate constants at different fluid flow situations should help to clarify the findings observed. Concluding, a model can be derived which allows the prediction of the monomer conversion in the process. Hence, technical applications of fore example shearing polymer solutions during reaction can be derived.

This investigation is still in progress and first results and considerations are presented here.

REFERENCES

[1] M. Vicevic, K. Novakovic, K.V.K. Boodhoo, A.J. Morris, *Chemical Engineering Journal* 135 **(2008)** 78–82.

[2] A. H. Navarchian, F. Picchioni, L.P.B.M. Janssen, *Polymer Engineering & Science* 45, **(2005)** 279–287.

[3] M. Buback, R. Gilbert, R. Hutchinson, B. Klumperman, F. Kuchta, B. Manders, K.O'Driscoll, G. Russell, J. Schweer, *Macromolecular Chemistry and Physics*, 196,**(1995)** 3267–3280

[4] S. Beuermann, M. Buback,G. Russell *Macromolecular rapid communications* 15**(1994)** 647–653

[5] N. Charton, A. Feldermann, A. Theis, M.Stenzel, T. Davis, C. Barner-Kowollik *Journal of Polymer Science Part A: Polymer Chemistry*, 42, **(2004)** 5170–5179

Your notes:

Impact of thermo-physical data on the modelling of high pressure polymerizations

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Nowadays modelling is a basic instrument for process optimization. Especially for technologies, which are conducted under exceptional process conditions, such as high pressure polymerizations, simulations are a welcome alternative to costly experiments in miniplants.

The synthesis of Low Density Polyethylene (LDPE) is an example for such an industrial process, which is typically operated between 100°C and 300°C and under pressures up to 3000 bar. The mathematical prediction of process parameters for the LDPE-Synthesis, for instance conversion, molecular weight distribution and branching, has been studied and refined since the early 1970s. By now the process simulation for LDPE synthesis poses a crucial tool for the LDPE-process development and optimization. But for the conduction of reliable and precise process simulations it is essential to have a very profound knowledge and understanding of the process itself, its thermodynamics and kinetics and of course the structure-properties relationship of the resulting polymer. Therefore a uniform set of parameters is essential, which can describe the polymerization reaction independently of reactor type and process. However this proves to be a highly demanding task as numerous parameters have to been known sufficiently precise within a complex reaction network and under the extreme process conditions. This is why variable parameters are still necessary in the current simulation models in order to obtain good agreement between calculation and plant data [1]. For tube reactors these parameters are e.g. the initiator efficiency and the thickness of the fouling layer inside the reactor.

The existence of these variable parameters as well as systematic discrepancies within the reactor models give reason for further investigations. In order to identify and overcome the knowledge gaps a systematic sensitivity analysis of the existing model concerning possible faulty parameters is the reasonable approach. Firstly the fundamentals, such as the thermo-physical properties, which serve as the basis of the polymerization model, should be revisited. For the simulation these are the

- density
- heat capacity
- viscosity and
- heat transfer coefficient

of ethylene, LDPE and the reaction mixture.

These data have to be available in dependence on temperature, pressure and composition, respectively. For the calculation of the viscosity molecular weight and branching structure of the polymer can also be taken into account. Whereas the density, the heat capacity and the thermal conductivity primarily influence the heat balance of the model, the viscosity of the reaction mixture also influences the kinetics directly. Reaction steps that depend on polymer mobility, such as the termination reaction of the polymerization, exhibit a direct dependence on the viscosity even at low polymer concentrations.

The literature on these properties for the pure components under process conditions is scarcely available and mostly dates back to the 1950s and 60s. Furthermore it often contains extrapolations and was analyzed with outdated mathematical methods. Experimentally based data on mixture properties is virtually inexistent, thus ideal mixing rules are applied without questioning [2], [3]. Moreover it becomes evident that some of the authors obtain differing values for the thermo-physical properties at a given temperature and pressure. Thereby the discrepancies reach up to several percent.

In the next step the impact of these parameters on the process simulation of high pressure polymerizations was studied and evaluated by the example of an industrial tube reactor.

Effects could mainly be observed in the resulting temperature profile and the achieved conversion. However these effects were negligible for the heat transfer, but conspicuous for the heat capacity and striking for the viscosities. For the heat capacity a constant error was introduced and evaluated. For small errors the adjustment of the variable parameters makes it possible to diminish the deviation caused by the introduced error to a minimum. This proves the concept of the variable parameters and explains why they sometimes exhibit physically unrealistic values.

But LDPE also possesses special rheological properties due to its unique branching structure. Thus the correct prediction of the molecular mass distribution as well as the polymeric microstructure is of striking importance for this polymer as well. Therefore it is also interesting to examine whether the viscosity of the reaction mixture, which directly influences the polymerization kinetics, shows any influence on the calculated molecular mass distribution and polymeric microstructure.

REFERENCES

[1] T. Herrmann, *Dissertation,* Darmstadt **2011.**
[2] A. Buchelli, M. L. Call, A. L. Brown, A. Bird, S. Hearn, J. Hannon, *Ind. Eng. Chem. Res.* **2005**, 44, 1474-1479.
[3] G. Luft, R. Steiner, *Chemiker-Zeitung* **1971**, 95 (1), 11-15.

Spectroscopic Investigations on a Redox Initiator System for continuous Emulsion Polymerization

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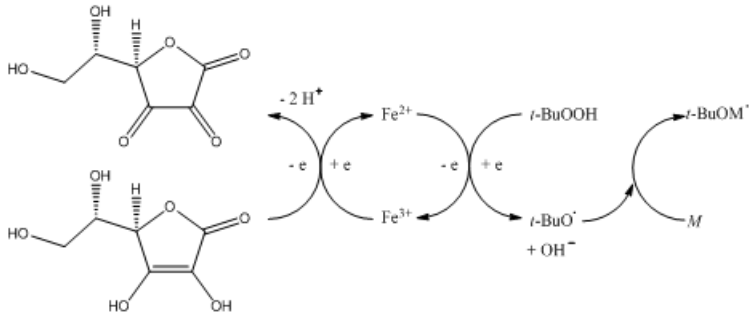
In emulsion polymerization, redox initiator systems offer advantages in comparison to thermal initiators, regarding to a faster radical production rate, the applicable temperature range as well as in terms of reaction safety.[1] For radical polymerization in tubular reactors, it is desirable to achieve a constant radical to monomer concentration throughout the whole length of the reactor. For this purpose, knowledge about the kinetics of the components is essential. In this work, results of kinetic investigations on the redox initiator system ascorbic acid/Fe3+/tert-butylhydroperoxide (TBHP) are presented. The main focus lies on the influence of traces of oxygen on the kinetics of the redox system.



UV/VIS Experiments on the decomposition time of the reducing agent -ascorbic acid- were carried out. It is shown, that the level of oxygen has a strong influence on the decomposition rate of ascorbic acid. The influence of TBHP concentration was investigated for different ratios of TBHP to ascorbic acid in the temperature range from 35 °C to 75 °C and ARRHENIUS parameters were determined. The complexity of the degradation mechanism hinders the development of generally valid mechanistic models.[2] Pseudo kinetic models such as zero- , first- or second-order kinetics are often applied. It is shown, that the experimental data can be described with a WEIBULL approach in a more appropriate way. Up to now, there is no data available regarding to the oxidizing agent. The cleavage of the TBHP O-O-Bond can be detected by Raman spectroscopy. Based on Raman spectroscopic data, a correlation between ascorbic acid and TBHP decomposition is possible.

REFERENCES

[1] N. K. Svelko, R. Pirri, J. M. Asua, J. R. Leiza.; Redox Initiator Systems for Emulsion Polymerization of Acrylates, Journal of Polymer Science: Part A: Polymer Chemistry, **2009**, 47, 2917–2927.

[2] M. C. Manso, F. A. R. Oliveira, J. C. Oliveira, J. M. Frías; *Modelling ascorbic acid thermal degradation and browning in orange juice under aerobic condi-tions*, International Journal of Food Science and Technology, **2001**, *36*, 303-312.

Your notes:

Modeling of the ring chain equilibrium in cyclic oligomers of polyethylene furanoate (PEF)

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The replacement of oil based chemicals by renewable resource based chemicals is one of the major issues chemical industry is facing right now. The alternative polymer polyethylene furanoate (PEF) is a possible substitute for polyethylene terephthalate (PET). It can be produced via ring-opening polymerization of cyclic oligoethylene furanoate (cyOEF). Several strategies can be used to produce these cyclic molecules from the two monomers furandicarboxylic acid (FDCA) and ethylene glycol (EG). We are exploring two promising routes which are depolymerization and reactive distillation, which are both techniques exploiting the ring chain equilibrium at high dilution. In both cases linear polymer chains of PEF are dissolved at high temperatures and reacted towards rings. This project is focused on the production of cyOEF using these techniques and the modeling of the ring-chain equilibrium of the cyOEF mixture.

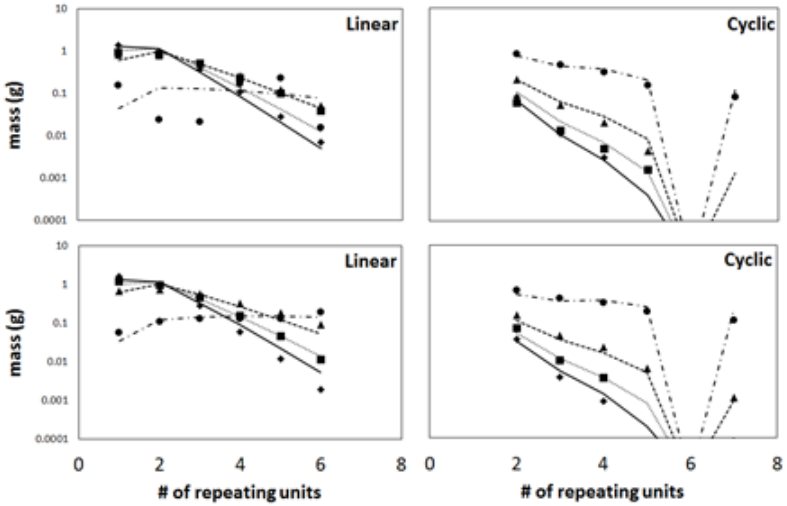

Figure 1. Comparison of experimental and model predicted cyclic and linear distributions at 2 different concentrations: 33 g/L (top) and 16 g/L (bottom). Data were taken at different molar ratios of EG to FDCA: 1:1 (●), 2:1(▲), 3:1 (■) and 4:1 (♦).

Under high dilution, the equilibrium shifts towards the ring-chain formation of cyclic oligomers. The equilibrium model of Jacobson and Stockmayer (JS), derived in the 1950s, can be used to predict this equilibrium for several types of polymers. It is based on computing the probability of ring closure using the assumption of a randomly coiled hydrocarbon chains for linear polymers.

Two fitting parameters can be adjusted in this model. One is the equilibrium constant K for the step growth polymerization, which is in equilibrium with the cyclization reactions. The second one is b, the effective link length of the bonds in the polymer chains. The latter is usually independent on the repeating unit. Experimental results from depolymerization and reactive distillation were fitted using the JS model (Figure 1). A typical distribution of cyclic oligomers has a dominant peak for cyclic dimer and is decreasing for cyclic trimers, tetramers, pentamers and so on. Interestingly, the cyclic hexamer does not appear at all. Since in our case the experimental distributions did not match the JS theory perfectly, the model was extended introducing a link length for every individual cycle. Using this adjustment, the fitting to experimental data could be improved significantly. These results suggest that it is indeed possible to use the JS theory to describe the ring chain equilibrium also for PEF. The model should be further generalized and made capable of predicting the actual effective link length, which is currently a fitting parameter. Such further improvements should enable the model to predict also the absence of cyclics with 6 repeat units, which was experimentally observed and has not been physically explained in the literature so far.

References

[1] Gandini, A., et al., *The Furan Counterpart of Poly(etylene terephthalate): An Alternative Material Based on Renewable Resources.* Polymer Chemistry, **2009**. *47:* p. 4.
[2] Burch, R.R., S.R. Lustig, and M. Spinu, *Synthesis of Cyclic Oligoesters and Their Rapid Polymerization to High Molecular Weigth.* Macromolecules, **2000**. *33*(14): p. 5053- 5064.
[3] Stockmayer, W.H. and H. Jacobson, *Intramolecular Reaction in Polycondensations. I. The Theory of Linear Systems.* The Journal of Chemical Physics, **1950**. 18(12): p. 7.

Your notes:

Tubular Reactor Concept for Process Intensification in Emulsion Polymerization

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Nowadays, most polymerization processes are carried out in batch or semi-batch. Due to their low surface to volume ratio and thus limited heat transfer capacity an intensification of highly exothermic polymerization reactions is limited in these reactors. [1] A tubular reactor is introduced which offers high potential for process intensification. The presented milli-sized reactor consists of a PTFE tube (10 m length; 10 mm inner diameter) and offers a high specific surface area. The integration of static mixing elements [2] in combination with secondary flow phenomena caused by the helical coiled structure of the tube [3, 4] leads to narrowed residence time distribution and an improved heat transfer. The potential for process intensification is shown by means of a case study for emulsion copolymerization reactions and cycle times up to 60 hours.

The use of PTFE as reactor material in combination with the reactor geometry enables the stable realization of copolymerization reactions in a wide range of solid content throughput of up to 40 per cent per weight without any form of polymer deposit on the reactor wall and therefor without changes in the reactor properties. Sampling and temperature measurement are allowed at various residence times without influencing the mass flow, thus the flow properties and the final product. [1] This allows to gather information about process and product as well as reaction properties e.g. temperatures, particle size, molecular weights at different reaction states.

The influence of the reaction parameters on the copolymerization process as well as on the polymer product itself has intensively been studied. The generated polymer and reactor data was therefore used for model development and validation with the objective of closed-loop control of the reactor. The reactor set-up and the case study emulsion show a good stability towards changes in feed composition and temperature disturbances in the inlet as well as in the jacket temperature of more than 15 °C. In a 62 h run the long term stability of the reactor was tested. The robustness of the system towards external disturbances allows a wide application range by means of online feedback control.

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[1] F. G. Lueth, W. Pauer, H.-U. Moritz, Properties of Smart-Scaled PTFE-Tubular Reactors for Continuous Emulsion Polymerization Reactions, *Macromol. Symp.* **2013**, *333*, 69–79.

[2] J. Schmidt, *Kinetische Und Reaktionstechnische Untersuchungen Zur Kontinuierlichen Schnellen Emulsionspolymerisation*; Moritz, H.-U., Ed.; Fortschrit.; Wissenschaft & Technik Verlag: Berlin, **2010**.

[3] M. Apostel, W. Pauer, H.-U. Moritz, J. Kremeskötter, K.-D. Hungenberg, The Wicker Tube Reactor - Characterization and Modeling, *Chim. Polym. React. Eng*. **2001**, *55*, 229–230.

[4] W. Pauer, H.-U. Moritz, Continuous Reactor Concepts with Superimposed Secondary Flow – Polymerization Process Intensification, *Macromol. Symp*. **2006**, *243*, 299–308.

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Your notes:

Analysis of the effect of Laponite® on Radical exchange in seeded semibatch Pickering Emulsion Polymerization

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"Pickering" stabilization of latex particles has recently emerged as a new method to create nanocomposite colloids by adsorption of solid particles at solid latex interfaces [1] and is named “Emulsion polymerization” by analogy to solid-stabilized emulsions [2]. The elaboration of composite latexes allows combining attributes of inorganic solids with the processing and handling advantages of organic polymers which allows for instance to improve mechanical and water-resistance properties in waterborne organic coatings[3].

The stabilization of polymer latex particles elaborated by Pickering polymerization mainly takes place by steric repulsions between adsorbed inorganic solid particles. The later form a rigid mechanical barrier that prevents the polymer latexes from coalescing. Electrostatic phenomena do not significantly contribute to the colloidal stability. However, the presence of inorganic particles at the surface of polymer particles might affect radical adsorption and desorption due to their charges or to the mechanical barrier. Therefore the growth step during the polymerization may be affected by the presence of inorganic particles.

In this work, we investigate the effect of Laponite® clays concentration on radical exchange, and therefore particle growth, in emulsion polymerization of styrene, in the absence of surfactant or other additives. Both experimental and modelling investigations are handled.

Seeded experiments were realized by varying the amount of Laponite®. The used seed was produced at 70°C using potassium persulfate as initiator in presence of a small amount of Laponite® (for nucleation and stabilization). The seeded experiments start in interval III, eliminating therefore the nucleation phase. Experiments presenting coagulation were also eliminated, to ensure constant particle number. The focus can therefore be made on particle growth and more precisely radical entry (absorption) and exit (desorption) from the latex particles. Experimental estimation of the average number of radicals per particle demonstrates that radical exchange plays an important role in Pickering emulsion polymerization. However, the Laponite® concentration does not seem to affect the growth rate.

In parallel, the effect of Laponite® concentration on particle growth was investigated by modelling, which allows estimation of adsorption and desorption parameters that are not available in the literature.

Smith and Ewart [4] first described the transfer of free radical activity into the interior of a polymer particle by direct diffusion of a free radical into a polymer particle:

$$R_c^p = 4\pi . r_p . D_w [R^w] . N_p = k_c^p . [R^w] . N_p$$

However, the diffusion theory only applies accurately to large uncharged particles. In order to apply this theory to smaller and charged particles, two additional phenomena must be considered: reversible absorption and electrostatic repulsion. For instance, free radical diffusion might be hindered due to the presence of anionic clay platelets on the surface of latex particles. With this modification, to be considered absorbed by the particles, a radical must propagate or terminate before eventual desorption. This is done by incorporating an efficiency absorption factor in the absorption equation (see Hansen and Ugelstad [5] [6] [7]). The net rate of radical absorption by a particle can be obtained from the following expression, accounting for the theory of mass transfer and the "absorption efficiency factor" Fp:

$$k_c^p = 4\pi . r_p . D_w . \bar{F_p}$$

Hansen and Ugelstad [7] also proposed an equation that combines the electrostatic repulsion factor, with capture reversibility to obtain the expression of Fp. Using this model, the electrostatic repulsion factor was estimated with varying Laponite® concentration in a way to fit experimental data. This again confirms that the Laponite® concentration does not affect the growth rate.

REFERENCES

[1] Bourgeat-Lami E., N. Sheibat-Othman, A. M. Dos Santos, in *Polymer Nanocomposites by Emulsion and Suspension*, V. Mittal, Ed., The Royal Society of Chemistry, UK, (2010), p. 269.
[2] Pickering, S. U. Emulsions. *J. Chem. Soc., Trans*. 1907, 91, 2001− 2021.
[3] A. Bonnefond, M. Paulis, S. A. F. Bon, J. Leiza, “Surfactant-Free Miniemulsion Polymerization of n-BA/S Stabilized by NaMMT: Films with Improved Water Resistance”, *Langmuir* 29 (7), 2397–2405, (2013).
[4] Smith, W. V., and Ewart, R. H. Kinetics of emulsion polymerization. The Journal of Chemical Physics 16, 6 (1948), 592–599.

Your notes:

Synthesis and characterization of emulsifier-free high solids content waterborne polymers

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Waterborne dispersed polymers are used in a wide range of specialty applications including coatings, adhesives, paper coating, additives for textiles and construction materials, impact modifiers for plastics and biomedical applications. Their market share is expanding with a forecast worldwide production of 13.3x106 tons (dry basis) in 2016 and an annual growth of 5%. These materials are mainly produced by emulsion polymerization and emulsifiers are the necessary evil in the process as they stabilize the otherwise unstable polymer particles in water. However, emulsifiers are deleterious for applications because they migrate during film formation increasing the water sensitivity, and reducing gloss and adhesion to substrates.

In this work, a process strategy for the production of emulsifier-free industrial–like (50 wt% solids) latexes has been developed. The core of the strategy is to incorporate charged moieties to the polymer backbone by copolymerizing minor amounts of sodium styrene sulfonate (NaSS) with the major monomers (methyl methacrylate, MMA, and butyl acrylate, BA). The charged moieties provide electrostatic stability to the polymer particles and as they are part of the long polymer chains, they do not migrate during film formation.

The challenge of the work relies in the fact that water soluble NaSS tends to polymerize in the aqueous phase. Therefore, its incorporation within poly(MMA/BA) chains is difficult. Through careful selection of the reaction pathway and optimization of the reaction parameters, coagulum-free latexes with controlled particle sizes were produced at high solids contents. The latexes were stable in a broad range of pH values. The application properties of these latexes and their films were evaluated by means of water sensitivity, gloss and mechanical tests and their performance was compared with control latex prepared by using conventional emulsifier.

Your notes:

New synthetic route towards anisotropic polymer-Gibbsite latex particles

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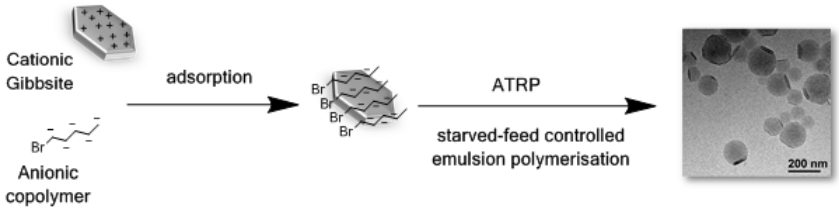
Currently, nanocomoposites, with an inorganic core and a polymer shell, represent significant class of materials which have diverse applications. Due to enhanced mechanical strength, stiffness, thermal, optical, and rheological properties, polymer-clay hybrid particles are widely used in coating technology [1]. Consequently, such a variety of improved properties can contribute to cost reduction. Even though free radical polymerisation is widely used for industrial production of nanocomposites, end products often have a high molar mass and broad molecular weight distribution. Therefore, in order to design novel materials with enhanced properties and controlled macromolecular architectures reversible-deactivation radical polymerisation should be used [2].

In this work, we present a new route towards the controlled synthesis of anisotropic polymer-Gibbsite latex particles via atom transfer radical polymerisation (scheme 1).



Scheme 1. Schematic representation of the synthesis of polymer-Gibbsite latex particles by aqueous starved-feed emulsion polymerisation using ATRP copolymers.

A random copolymer consisting of acrylic acid and butyl acrylate units was synthesised by using ATRP. It was used as a stabiliser for Gibbsite platelets and macroinitiator for copper(II)-mediated starved-feed emulsion polymerisation. By a careful selection of hydrophobic ligand, feeding profile of reducing agent and copper(II)/reducing agent ratio, for the first time, successful ARGET ATRP emulsion polymerisation was conducted in a control way using anionic surfactant without any additives. Cryo-TEM characterisation revealed muffin-like morphology of the resulted composite latex particles. Monomer feed composition and its feeding profile did not affect particles morphology. With this new route we can achieve control in the orientation of the Gibbsite platelets and avoid any chemical modification of the inorganic particles surface prior to the polymerization.

REFERENCES

[1] T. Sugama, Materials Letters, 2006, 60, (21-22) 2700 -2706.
[2] M.K. Georges, R.P.N. Veregin, P.M. Kazmaier, G.K. Hamer, Macromolecules, 1993, 26, 2987-2988

Your notes:

How to go full circle from polymerization kinetics (fundamentals) to final desirable application properties (applied engineering)?

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Among water-soluble polymers, copolymers of acrylamide (AAm) and acrylic acid (AAc) are probably the most common and widely used. One important application of AAm/AAc copolymers with growing interest in both fundamental and applied areas is in enhanced oil recovery (EOR). In order to increase the efficiency of oil recovery by polymer flooding techniques, it is needed to have well-designed polymers with desirable properties. Since application properties are tied to the microstructure of the copolymer, which is in turn related to the underlying kinetics of the copolymerization, systematic kinetic studies provide a better understanding of possible influential factors in copolymerizations and copolymer properties. However, information on the kinetics of the AAm/AAc radical copolymerization is rather scarce.

The first stage to tailor-make polymers for EOR application was to clarify monomer reactivity ratios, which are very inconsistent in the literature, and to proceed with an optimal approach to estimate reliable reactivity ratio values.

Secondly, a systematic study was conducted on AAm/AAc copolymerization kinetics to investigate the effects of various factors such as pH, ionic strength and monomer concentration, on different responses, such as monomer reactivity ratios, monomer conversion, copolymer composition, monomer sequence length, and polymer molecular weight, in order to understand the relationships between copolymerization kinetics and copolymer microstructure.

After clarifying the polymerization kinetics, in the third stage, it was aimed to modify copolymer properties such as polymer molecular weight, copolymer composition, sequence distributions of monomers along the copolymer chain, and shear viscosity. Therefore, the prior systematic study of copolymerization kinetics and copolymer properties provided us with the required understanding of possible influential factors in both recipe and operation conditions. Based on this knowledge (structure-property relationships), tailor-made AAm/AAc copolymers with the desirable properties were designed for EOR applications.

In the fourth and last stage, we evaluated the EOR performance properties of copolymers. The copolymer performance was evaluated and compared with a commercially available copolymer of the same type that is currently used in oil reservoirs. The results showed a noticeable improvement in the behavior of our tailor-made copolymers in improving mobility control and effective viscosity and decreasing polymer retention in the porous media.

The amounts of original oil in place (OOIP) recovered by the tailor-made copolymers were higher than those with the commercial copolymer, thus representing higher oil recovery efficiency for the designed copolymers. In addition, less volume of water was required and produced in the heavy oil displacement tests for the tailor-made copolymers compared to the reference copolymer. This can decrease the operational costs for water handling, recycling or disposal according to environmental regulations in oil fields.

This study gave a perfect representation of how to go full circle from copolymerization kinetics (fundamental phase) to the final desirable application properties (applied engineering phase) to tailor make polymers with enhanced properties in order to increase the efficiency of oil recovery and decrease the amount of water use in oil reservoirs.

Your notes:

Triboelectric charging of polyethylene

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Triboelectric charging or triboelectrification can be briefly defined as charging of bodies caused by their mutual friction. Although this phenomenon has been observed for many centuries, the progress in understanding of the actual charging mechanism mainly in the case of insulator charging is unsatisfactory. Aside from everyday activities like combing hair or driving a car, triboelectrification frequently happens in industrial processes, mainly when dealing with powders. Specifically, during powder processing and production the contact of the particles with a device wall as well as the mutual particle collisions cause electrons on the particle surface to redistribute in such a manner that the particles become charged. Such charged particles often cause operational problems due to unwanted particle aggregation or segregation and also pose safety risks due to potential sudden discharge. We focus especially on fluidized bed polymerization reactors, where charged polymer particles form aggregates and wall sheets, which at least negatively affect the optimal flow regime and at worst choke up the reactor, resulting thus in the reactor shutdown.

Our objective is to better understand the process of charging on the level of particle-particle and particle-wall interactions. Unfortunately, experimental results in literature range significantly and often lack a systematic approach. It is mainly the result of complications in manipulation with the dielectric powders, since even a small change of the particle surface or friction caused by manipulation with the powder can alter experimental results. Also, the charge decay times are sometimes extremely long, which to a certain extent prohibits repeated measurements on identical sample. Our systematic series of experiments aimed at investigation of charging dynamics of polymer particles allowed us to develop a mathematical model of the charging dynamics on the level of particle ensembles.

The 'cascade method' apparatus, that is a slide followed by the Faraday's pail, was utilized in order to observe the particle-wall charging of polymer powders in friction contact with various materials. Our simplified mathematical model of colliding polymer particles in fluidized bed polymerization reactor employs the Discrete Element Method (DEM) to describe the particle dynamics and incorporates trapped electron balance as the physical basis for the charging mechanism.

Our results show that the charging dynamics due to the particle-wall contacts follows a saturation curve corresponding to the maximum charge under considered conditions. After fitting the curve we show that the charging is proportional to the difference in effective work functions of the materials in contact. The fitting equation contains charging constants. We determine the charging constants dependency on several parameters, namely on humidity, material of the slide or walls and particle size distribution. Unlike the results one can find in some of the electrostatics involving publications, we observe significant charging even in the case of the same materials being in contact, for example polyethylene particles with polyethylene wall. Based on these experimental observations, our simplified DEM model provides predictions of particle charge distribution in the reactor for a range of parameters, i.e., reactor temperature, particle volume fraction, particle size distribution and the level of particle segregation. In the case of polymer particle-particle interaction in polydisperse systems, big particles tend to gain positive charge and small particles the negative one. The wider is the particle size distribution the more pronounced is the charging process. Based on our experimental and modeling studies we discuss various possibilities of charge neutralization and control of the charging dynamics.

Your notes:

Kinetics of a multi-stage polymerization of olefins in a single reactor setup

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Introduction

About 50 % of the world plastic demands are polyolefins, mostly Polyethylene (PE) and Polypropylene (PP). It is used in a wide field of applications, for low cost products in packaging as well as high end applications like water pipes and constructive parts in the automotive industry. Over the last years the properties of polyolefins and their control have been improved, which allows the substitution of other plastics and even other materials. Further advantages are the low cost of production, the easy accessibility of the feedstock and an easy way of recycling.

Experimental

The approach in this work is to achieve kinetic data of the polymerization of PE, PP and EPR (figure 1) in a single batch reactor setup. In a first step a homo-PP is produced in slurry polymerization. For the second step the solvent is flushed and the reaction is continued in gasphase with co-monomer and hydrogen. Further incorporation of PE in a PP matrix is possible to get EPR rubber. By this procedure industrially relevant multi-reactor polymerizations can be mimicked in a single bench scale batch reactor and kinetic data of the polymerization process can be obtained.

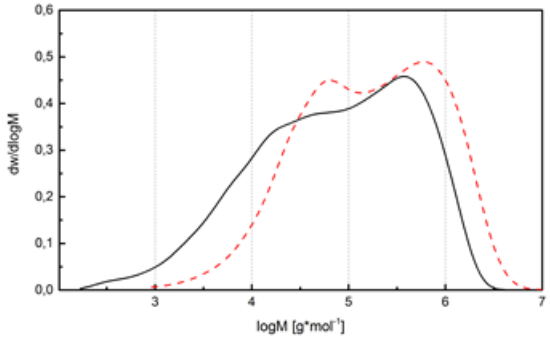

Figure 1: Molecular weight distribution of two typical bimodal PEs.

Results

Different types and amounts of co-monomer and co-catalyst have been used to investigate the influence on the kinetics of a state-of-the-art industrial Ziegler-Natta catalyst system. Furthermore the obtained powders are characterized by means of DSC and GPC for investigation of the co-monomer content in the multimodal polymer. The morphology of the obtained polymers is characterized by SEM.

Your notes:

Experimental Investigation of Z-N Catalyst Pre contacting on Polymerization

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Polyolefines account for about one third of the plastics production, with heterogeneous Ziegler-Natta (Z-N) based catalysts dominating the polyolefin production. Since the first Z-N polymerization in 1953 by Karl Ziegler and his research team, there is a constant progress in catalyst design to increase the catalyst activity and powder morphology [1].

Beside the catalyst design there are further possibilities to enhance a catalyst system. It is described that pre-treatment of the catalyst can influence the activity of the catalyst system and particle morphology [2]. Especially co catalyst (aluminium alkyl) diffusion into the catalyst particle is very important for the catalyst activation, like described in Figure 1 [3].

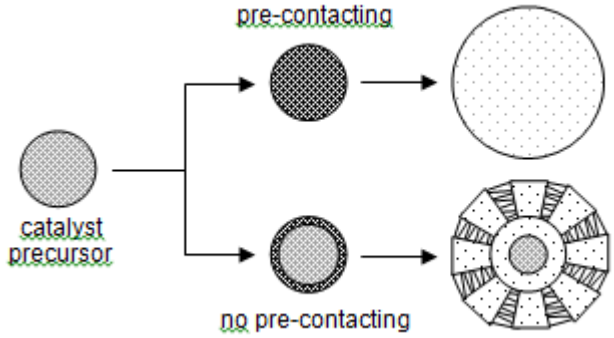

Figure 1: Illustration of pre-contacting effect on morphology and activity.

The influence of pre-contacting on a heterogeneous Ziegler-Natta catalyst was investigated under different polymerization conditions. Therefore polymerization experiments of ethylene and in addition with 1-butene/1-hexene as co-monomer were performed in a 0.5 l reactor. Furthermore several parameters like pre-contacting time, ethylene/hydrogen concentration, and mixing have been varied to study their effect. The received polymer powders were analyzed for their properties.

The ideal duration of pre-contacting time increased the activity of a Z-N catalyst by 25-40 %. Additionally the fractioning behavior of the catalyst was related to the pre-contacting time. As a result the pre-contacting time seriously influenced the particle morphology.

References

[1] Galli P., Vecellio G., Technology: driving force behind innovation and growth of polyolefins, *Progress in Polymer Science,* (**2001**), *26*(8), 1287–1336.
[2] Daftaribesheli M., Comparison of catalytic ethylene polymerization in slurry and gas phase, (**2009**), University of Twente, Enschede.
[3] Nooijen G., On the importance of diffusion of cocatalyst molecules through heterogeneous ziegler/natta catalysts, *European Polymer Journal,* (**1994**), *30*(1), 11–15.

Your notes:

The Effect of Silica Dehydroxylation Temperature on Catalytic Performance of supported (n-BuCp)2ZrCl2 in Ethylene Polymerization

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Amorphous silica is among the most common, and widely investigated catalyst support in the polyolefins industry. In particular, metallocenes are supported on pure, or amorphous silica modified with different types of cocatalysts (e.g., methylaluminoxane (MAO), Triisobutyl aluminium (TIBA) etc.) or spacer groups (e.g., n-BuSnCl3 etc.) to prepare supported catalysts which are then employed in industrial processes to produce different grades of polyolefins. The surface of untreated silica contains water, geminal, vicinal and isolated hydroxyl groups, collectively known as silanols. It is well known that the surface concentration and nature of silanol groups can be altered by the thermal and/or chemical treatment of the silica. However, it is difficult to establish the nature and concentration of the silanol groups at the silica surface that are most suitable for a specific metallocene for the generation of an active metallocenium cation and thus, for the optimal catalyst performance.

The objective of the present study is to investigate the effect of silica dehydroxylation temperature on the catalytic activity of Grace 948 silica supported (n-BuCp)2ZrCl2 metallocene in ethylene polymerization. Dehydroxylation temperatures considered are 200°C, 450°C and 600°C covering the commonly used temperatures range for silica supported metallocenes. Two synthesis methods have been used for supported catalysts: i) by grafting (n-BuCp)2ZrCl2 on silica modified by MAO and ii) by grafting (n-BuCp)2ZrCl2+MAO solution on silica. Furthermore, the polymerizations have been carried out both in slurry and gas phase processes by using two types of scavengers i.e., Triethyl aluminium (TEA) and Triisobutyl aluminium (TIBA). Finally, the influence of silica dehydroxylation temperature on molecular weight distribution (MWD) and crystallinity of the obtained polyethylene samples have been analyzed.

The obtained results show that for catalysts prepared with method 1, Aluminium content of the silica (dehydroxylated at different temperatures) after impregnation of MAO reduced with increasing the dehydroxylation temperature which can be attributed to decrease in Si-OH concentration. For catalysts prepared with method 2, Aluminium and Zirconium content of the catalysts remained almost constant. The intrinsic and average activity of silica supported (n-BuCp)2ZrCl2 in ethylene homo & copolymerizations was observed to increase with increasing silica dehydroxylation temperature from 200 to 600°C, both in slurry and gas phase processes (see Figure 1) for both types of catalyst synthesis methods. The same trend was also observed by using two different alkyl aluminiums (i.e., TEA and TIBA) as scavengers. However, MWD and crystallinity were found to remain unaffected by the silica dehydroxylation temperature.

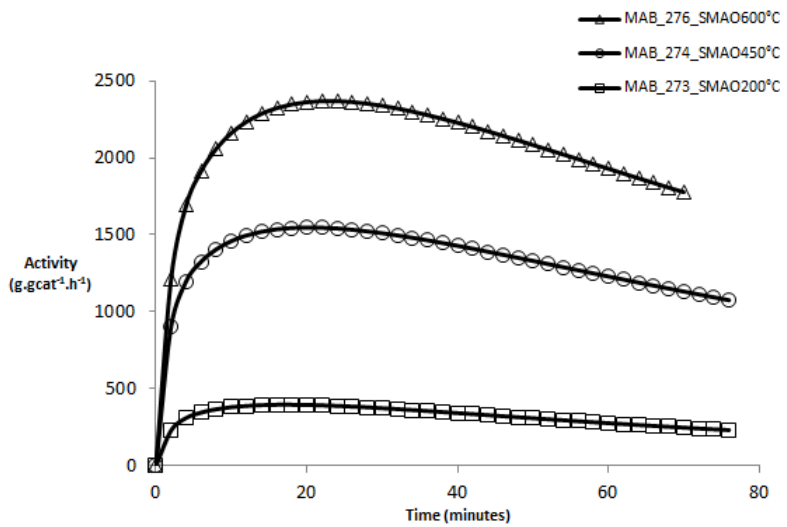

Figure 1. Comparison of slurry phase homopolymerization kinetic profiles of catalysts prepared with different silica dehydroxylation temperature using method 1 and TIBA as scavenger.

Acknowledgement:

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Your notes:

A Novel Approach to Determine Partition Coefficients of Monomers in Polymer Dispersions via Headspace Gas Chromatography

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Dispersion polymerization is a heterogeneous polymerization process carried out in the presence of a polymeric stabilizer within the reaction medium. Polymerization processes leading to the precipitation of polymer chains have been studied over the last five decades [1]. Dispersion polymerization – usually carried out in organic solvents – is especially useful to produce particles in the order of a few micrometers [2], closing the gap between emulsion and suspension polymerization [3]. Applications range from chromatography packing materials [4] to liquid crystal display spacers [5]. To model the reaction kinetics, many different aspects have to be considered: the contributions of the reaction in both reaction loci (continuous and dispersed phase), the kinetics of the polymer build-up and the evolution of the particle size distribution. One of the most important aspects of such models is the accurate description of the interphase partitioning of the different reactants (with special emphasis on the concentration of the monomers in the polymer phase) as well as a thorough evaluation of the compatibility between the polymer and the selected reaction medium. The aim of this work is to assess the potentials of headspace gas chromatography (HSGC) as a fast and reliable technique to fully characterize the thermodynamic behavior of the polymer dispersion with a reasonable experimental effort and using small amounts of raw materials.

With reference to a two-phase system involving solvent- and polymer-rich phases, a step-by-step procedure has been developed to explore all partitioning aspects in the general multicomponent case (several monomers, two solvents).

As first step, the activity is determined for each two-component mixture of all the involved species. This is done by preparing a series of samples with changing molar composition, heating them up to the desired temperature, leaving them for equilibration and subsequently sampling the gas phase in equilibrium with the liquid phase. The areas of the relevant peaks obtained via GC (e.g. with a flame ionization detector (FID)) are divided by the areas obtained for the pure components. This ratio is defined as the activity of a two-phase mixture. A suitable thermodynamic model is used to correlate the activity and the liquid phase molar composition.

In a second step, a series of vials is prepared with a constant amount of dry polymer. To each of these vials, an increasing amount of the two-component solution with specific composition is added. These samples are also measured by HSGC and the activity is recorded. Using the thermodynamic model, the corresponding molar fraction of the two components is determined. As long as the sum of these two molar fractions is below 1, the liquid phase is non-existent.

On the other hand, the polymer phase is saturated and the first droplet of the liquid phase is formed at the moment where the sum reaches 1. This way, the amount of solution at the selected composition required to saturate the polymer phase is readily evaluated. This step is repeated with solutions at different composition while recording the amount of solution at saturation. Eventually, these amounts as well as their compositions can be plotted versus the liquid composition of the added solution: these data are used to evaluate the monomer/solvent partitioning between liquid and polymer phases again using suitable thermodynamic models. In the simplest case, partition coefficients can be used.

The procedure outlined above will be demonstrated with reference to specific systems typical of dispersion polymerization.

REFERENCES

[1] Barrett, K.E.; Thomas, H.R. *J. Polym. Sci. Part A* **1969**, 7, 2621.
[2] Ober, C.K.; Lok, K.P. *Macromolecules* **1987**, 20, 268.
[3] Kawaguchi, S.; Ito, K. *Adv. Polym. Sci.* **2005**, 175, 299.
[4] Richez, A.P.; Yow, H.N.; Biggs, S.; Cayre, O.J. *Prog. Polym. Sci.* **2013**, 38, 897.
[5] Zhang, X.; Boissé, S.; Bui, C.; Albouy, P.; Brûlet, A.; Li, M.; Rieger, J.; Charleux, B. *Soft Matter*, **2012**, 8, 1130.

Your notes:

Open- and closed-cell polystyrene foams prepared by thermally induced phase separation

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The preparation of polymer foams with varying morphologies opens new application potentials since their morphology affects their physical properties. Nowadays, polystyrene foams (PS) are produced with a closed-cell structure. We studied both experimentally and by modelling the liquid-liquid phase separation (thermally induced phase separation, TIPS) resulting in foam formation (without blowing). The TIPS method enables to prepare foams with open- or closed-cell structure and even with their combination. We focused on the system consisting of PS and two different solvents, namely cyclohexane and cyclohexanol.

First, the foams were prepared in the in-house made apparatus. Then, the resulting foam morphology was analysed and characterised by mercury porosimetry, SEM (Fig. 1a, 1b) and image analysis. Moreover, we measured the binodal curves (cloud-points) by a thermo-optical method again with the in-house made apparatus.

In the modelling effort, we employed the Cahn-Hilliard approach suitable for systems where phase separation takes place by the mechanism of spinodal decomposition. The model is based upon thermodynamics given by the Flory-Huggins theory. The polymer-solvent interaction parameter was obtained from the Hildebrand solubility parameters with Hansen dissipation contribution and was validated against cloud-point experimental data. The interfacial tension parameter was validated indirectly from auxiliary experiments. The model predicts correct length scales of open- and closed-cell morphologies for a variety of system compositions and temperatures. Fig. 1c shows a 3D profile with cell sizes similar to experimental ones in Fig. 1b.

Both experiments and model provided three types of morphologies: (i) polymer particles dispersed in solvent, (ii) open-cell morphology of two co-continuous structures and (iii) closed cells of solvent in continuous polymer. As a fourth morphology their combination, i.e., the open-cell structure with closed cells in the walls, was obtained. The foamed materials exhibit best mechanical properties when produced with composition that is comparable to the critical composition, and this was confirmed by experimental results as well as 3D model predictions.

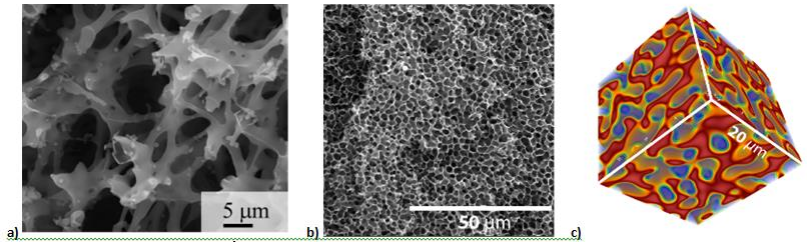

Figure 1: PS foams with a) open cells, b) closed cells and c) model-predicted 3D morphology of the foam comparable to Fig. 1b.

Your notes:

Thermodynamics of sorption and swelling in polyethylene under gas- and liquid-phase polymerization conditions

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Thermodynamics of sorption and diffusion of monomer(s) and/or diluents in semi-crystalline polyolefins is one of the important phenomena affecting catalytic polymerization processes, down-stream processing as well as application properties of these materials. Despite the importance, thermodynamically consistent and predictive tools for sorption equilibria are available only for a few specific cases and the attempts to predict the swelling of semi-crystalline polyolefins using equations of state have not been successful so far. Prediction of diffusion in polyolefins is another open problem. This situation is caused by several reasons: (i) scarce experimental data for the broad range of various PE grades, temperature, pressure and composition of penetrant mixtures, (ii) elastic constraints affecting the thermodynamics of amorphous phase, (iii) alternative interpretations of the semi-crystalline morphology of lower crystallinity PE, (iv) temperature-dependence of crystallinity, and (v) number of inter-connected phenomena affecting the diffusion of penetrants in polyolefins.

In this contribution we are going to concentrate on the swelling of various PE grades for a broad range of temperatures, pressures and penetrants. The reason is the limited amount of experimental data on swelling since the few conducted experimental investigations have been limited to a narrow range of samples and conditions. Another reason is the difficulty to accurately predict the density of condensed phase (including the swelling) by the thermodynamically consistent approaches. We present a comprehensive experimental study of the swelling induced in various grades of PE particles by the sorption of ethylene, co-monomers (1-hexene, 1 butene) or inert diluents (propylene) during gas-phase polymerization. Experiments were carried out at various temperatures and pressures in a custom-designed video-microscopic apparatus. The swelling data were evaluated using image-processing software and compared with the corresponding sorption isotherms. The results of swelling and sorption measurements in gaseous and liquid penetrants are interpreted in the context of our recently proposed phase structure of PE (Polymer 2015, 58, 189-198).

Your notes:

Process design for sulfuric acid leaching of iron bearing slags

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It was previously shown that different valuable metals can be leached from iron silicate slags under sulfuric acid conditions without gel formation.[1] This work focuses on process optimization by evaluation of kinetic data and improvements of process design.

The influence of crystallinity of slags cooled fast and slow on the leaching behavior was compared. Fast cooled slags usually prevent a good crystallization producing an amorphous phase and can be leached faster under the same or even more moderate conditions. Another important factor on leaching kinetics is the chemical composition of the slag. By investigation of the leaching behavior of iron silicate slag and converter slag due to the chemical bonding, it was observed that iron silicate dissolves significantly faster than converter slag, which has the iron oxide as major component..

The potential market price of the products obtained from the valuable metals in the leachate, including the transformation costs metal into product, served for the estimation of process economics. For this particular case of iron, the production of iron sulfate and iron oxide was compared. The market for these two products is completely different regarding technical and quality requirements.

The potential environmental impact of the process was studied by analyzing the leaching behavior of environmentally relevant elements such as arsenic and lead. Furthermore the process steps with high energy consumption were studied more closely in order to reduce the energy requirement (e.g. reaction parameters to obtain filtration cakes with lowest moisture; drying process of wet filter cakes).

REFERENCES

[1] J.H.-Redmann, *Entwicklung eines Verfahrens zur Extraktion von Wertstoffen und zur Herstellung von Eisenverbindungen aus Eisensilikatgestein,* Dissertation, Universität Hamburg*,* **2014**.

Your notes:

Application of Zirconocendichlorid in the Ethylene Polymerization under High Pressure Conditions

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In industry there are two relevant modes to polymerize ethylene. These provide products of different microstructure, which has a significant impact on the physical and mechanical properties of the resulting polyethylene. The free radical polymerization of ethylene in a high pressure process (1500-3000 bar) gives a product which microstructure consists of random distributed short (SCB) and long (LCB) chain branches. The latter affect the rheology of the polymer and improves its processability. On the other hand SCBs cause low densities and crystallinities. Therefore the product of the high pressure process is known as Low Density Polyethylene (LDPE).

The second industrially relevant mode for ethylene polymerization is the coordinative polymerization by transition metal catalysts at a medium pressure range (14-69 bar). Industrially heterogeneous Ziegler Natta and homogeneous metallocene catalysts are used to polymerize ethylene. The product microstructure is linear with practically no branching. Due to the lack of SCBs it has higher densities than LDPE and is therefore referred to as High Density Polyethylene (HDPE).

HDPE has some advantages compared to LDPE concerning its mechanical and physical properties. For example it has a higher tensile strength and is more resistant at higher temperatures. However, the improved mechanical and physical properties occur at the expense of the polymer processability. One possibility to counteract this disadvantage is the introduction of LCBs. This can be achieved by using special catalysts, which are able to incorporate a terminated polymer chain as macromonomer into the growing polymer chain. The best known example for this, are the constrained geometry catalysts (CGC-catalyst). However specific bridged catalysts on the basis of metallocenes are also known to produce PE with LCBs.

High pressure conditions can have a crucial influence on the catalytic polymerization of ethylene. The work of Luft et al.[1] indicated that high-pressure conditions lead to an increase in catalyst activity and molecular weights. In this context the question arises, which impact high pressure conditions have on the formation of LCB.

REFERENCES

[1] J.H.-Redmann, *Entwicklung eines Verfahrens zur Extraktion von Wertstoffen und zur Herstellung von Eisenverbindungen aus Eisensilikatgestein,* Dissertation, Universität Hamburg*,* **2014**.

In order to investigate the influence of high pressure conditions on the LCB, four bridged metallocene catalysts were chosen for testing. However, the first task is the development of an experimental procedure for the high pressure polymerization of ethylene by metallocene catalysts. For this purpose, the commercially available unbridged metallocene catalyst $ZrCp_2Cl_2$ is used. At the same time it can serves as reference for coming studies. The experimental setup for this study is a continuous high pressure polymerization plant. It is constructed for pressures up to 2500 bar and temperatures up to 300°C.

REFERENCES

[1] A. Rau, et al., Chemical Engineering & Technology, 2002, 25, 494-498.

Your notes:

Modelling of technical reactors for the production of ethylene copolymers

Sascha Griebenow, Markus Busch, Technische Universität Darmstadt.

The free radical high-pressure polymerization of ethylene has been used in industry for years to produce low-density polyethylene (LDPE) and ethylene copolymers. These processes are characterized by high reaction temperature (150 – 300 °C) and pressure (1000 – 3000 bar). The reaction mixture behaves as a supercritical fluid, with polymer soluble in the unreacted monomer under most operating conditions. Both stirred autoclave reactors and tubular reactors are commonly used in the industry. It is known that polymers manufactured by these processes differ in their molecular architecture and many of the important application properties. Polymers produced in autoclave reactors are more hazy than those produced in tubular reactors and suitable for extrusion coating and molding applications. The simulation of existing industrial reactors is an important tool to understand the processes inside the reactor. This knowledge helps to optimize industrial facilities or to plan the construction of new industrial reactors. Without cost- and time-intensive experiments the simulation allows to investigate product-oriented recipes in advance. Additionally the knowledge of the processes inside the reactor results in a better risk assessment and thereby leads to an increase in safety.

The aim of this scientific work is the development of a model. It should be able to describe a free radical high pressure copolymerization in a technical autoclave reactor. Beside the simulation another target is to evolve a gel permeation chromatography (GPC) method to measure the molecular weight distribution and the composition of the copolymer as a function of the elution volume.

To detect the molecular weight distribution a light scattering detector (LS) is used and is combined with an infrared detector (IR) which detects the composition of the eluted polymer.

Your notes:

Investigation of the Redox-Initiated Polymerization in Levitated Single Droplets

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In the chemical, pharmaceutical and food processing industries, spray processes have a wide range of applications, especially in the production of powder products from solutions or suspensions. In the case of spray polymerizations, the influences of process parameters like temperature and relative humidity on the polymerization process itself as well as on the physical properties of the product are of great interest.

The processes can be affected by varying the spraying parameters, such as temperature and humidity. The investigation of processes inside a single droplet (e.g., reactions, mass and heat transfer) in a spraying process is only possible with disproportional apparatus expenditure. However, the study of such processes is essential in order to achieve an optimization of product properties and process parameters.

In this study, an acoustic levitator was used to investigate the polymerization of a fast reactive system in order to take a closer look at the competitive characteristics of evaporation and polymerization in levitated droplets (Fig. 1). Online analyses of the redox-initiated polymerization were performed by shadowgraphy[1] and Raman spectroscopy[2] simultaneously. The initiator system consisted of ascorbic acid/Fe2+/3+/peroxide. Shadowgraphy was used to monitor the evaporation of the droplet. Raman spectroscopy was used to improve the knowledge of the influence of the exothermic polymerization on the evaporation and to monitor the progress of the free radical polymerization. The dried particles were investigated by scanning electron microscopy (SEM).

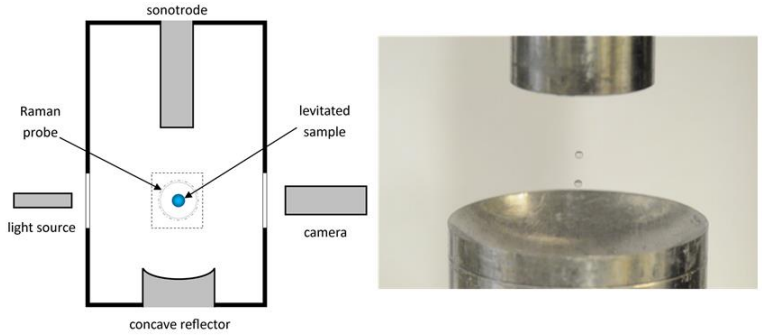

Figure 1: a) Process chamber of the acoustic levitator with the Raman probe in the background outside the chamber, b) levitated droplets.

REFERENCES

[1] H. Grosshans, M. Griesing, S. Gopireddy, W. Pauer, H.-U. Moritz, E. Gutheil Numerical and Experimental Study of the Evaporation and Solid Layer Formation of a Bi-Component Droplet Under Various Drying Conditions, *ASME*, **2014**.
[2] J. Laackmann, Aufbau und Automatisierung einer Versuchsapparatur zur Untersuchung der radikalischen Polymerisation in akustisch levitierten Einzeltropfen am Beispiel von N-Vinyl-2-pyrrolidon, University of Hamburg, **2014**.

Your notes:

Polymer foams with improved heat insulation properties

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The morphology of polymer foams determines their application potential. Polymer foams can have various foam morphologies- open-, closed- and the combination of open- and closed-cell structures. This variety enables a wide range of applications. Mastering the control of the foaming process and thus the preparation of desired foam morphologies is the key to the production of materials with improved properties.

In this work, we focused on foams with improved heat insulation properties. Foams with improved heat insulation properties can be obtained, for example, by decreasing the cell size below 10 µm while maintaining the porosities higher than 90 %. Commercial foams such as polystyrene (PS) and polyurethane (PU) have the cell size larger than 100 µm. By a deeper understanding of processes during foaming such as nucleation, coalescence and phase separation, we can better control the process and thus to decrease the cell size.

We experimentally studied the before mentioned processes on PS foams prepared by pressure and laser induced foaming, thermally induced phase separation, and on PU foams. The morphology analysis is in this case the alfa and omega and therefore we place the emphasis on measuring the samples by various methods and the advanced image analysis. For the foam analysis we used SEM, AFM, X-ray micro-tomography, He pycnometer, Hg porosimeter and we made preliminary measurements of heat insulation properties. By optimizing the foaming conditions we were able to prepare PS foams with various morphologies and with the cell size below 10 µm while the porosities were higher than 90 %.

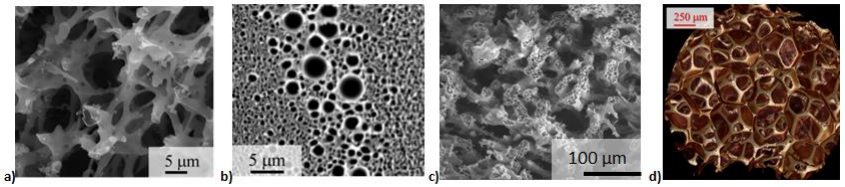

Figure: PS foams with a) open cells, b) closed cells, c) the combination of open and closed cells in their morphology and d) 3D morphology of a PU foam.

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