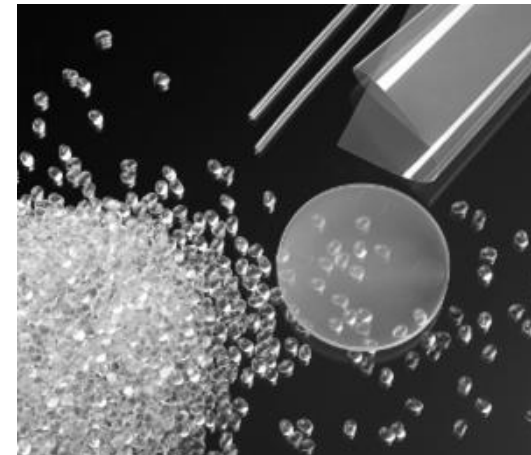


# Conference Guide

3<sup>rd</sup> PhD-Workshop on Polymer Reaction Engineering

12<sup>th</sup>-14<sup>th</sup> September 2014 in San Sebastián



[http://www.efce.info/PhD\\_Workshop+of+WPPRE.de](http://www.efce.info/PhD_Workshop+of+WPPRE.de)

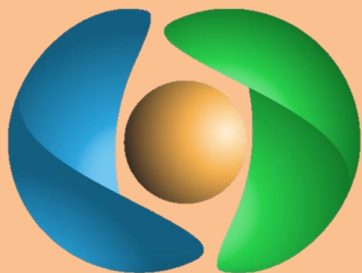


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# Welcome to the 3<sup>rd</sup> PhD-Student Workshop on Polymer Reaction Engineering

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 third 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 last year and involved 43 people. This year we are recording a maximum number of registrations.

Just as the participant number is increasing from year to year we are also trying to continuously extend the scope of research fields covered in the oral presentations and poster contributions. This year you can look forward to contributions concerned with:

- 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

- packaging and biomedical applications
- results obtained by new analytical methods

Having all these wonderful topics up in our sleeves we are looking forward to an interesting workshop in San Sebastián with you.

The Organizing Committee

## Organizing Committee

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Markus Busch	Chair of WPPRE, TU Darmstadt
Werner Pauer	Secretary of WPPRE, University Hamburg
Jose R. Leiza	POLYMAT, University of the Basque Country
Claudia Schwartzkopff	TU Darmstadt
Amaia Agirre Iribarren	POLYMAT, University of the Basque Country
Ines Plaza	POLYMAT, University of the Basque Country

## Sponsors

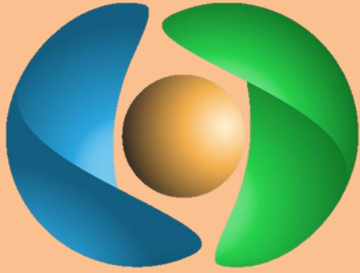
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# Arrival in San Sebastián

## Public Transport into the city & Your way to the workshop

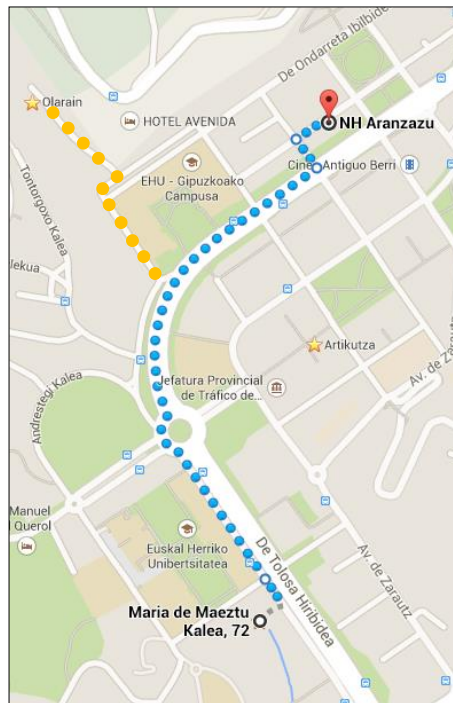
### Transfer from the airport into the city

Once landed in Bilbao there is the possibility to take a bus to the city center of Donostia/San Sebastián. The bus PESA departs at the station 'Termibus' at the airport and takes between 1 hour and 1,5 hours for the transfer depending on the traffic. The final stop in San Sebastián is a central bus station (see the labels in the map on the right).

If you want to go to the Olarain residence or the NH Aranzazu, you should use the bus lines 24 or 27, which depart at the other side of the roundabout.

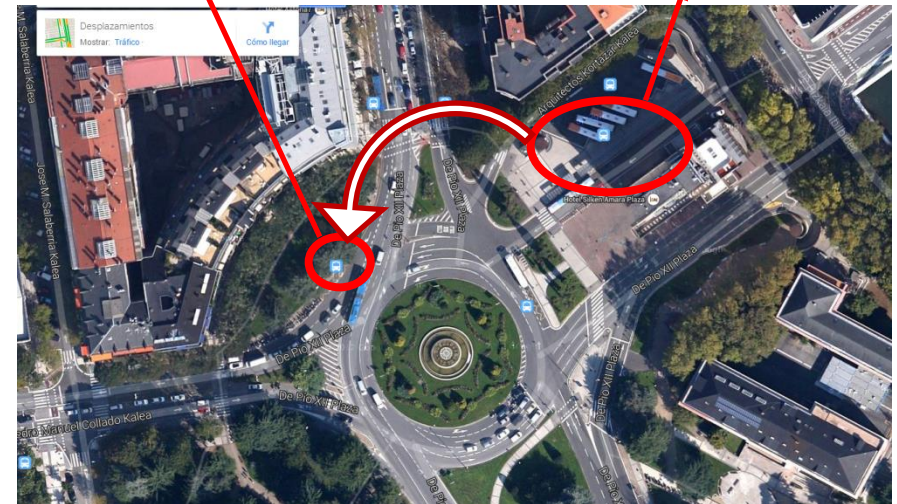
### The way to the workshop

The Joxe Mari Korta Center, where the PhD-workshop is going to take place, is within a 10 minute walking distance from both hotels.



Bus lines to go to  
OLARAIN and NH Aranzazu.  
Bus stop: PIO XII

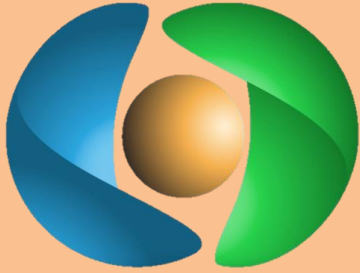
Central bus station  
Final stop of airport bus



### Contact

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

wpre@chemie.tu-darmstadt.de  
[http://www.efce.info/PhD\\_Workshop+of+WPPRE.de](http://www.efce.info/PhD_Workshop+of+WPPRE.de)



# General Information

## Language

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The official language at the workshop is English.

## Internet

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You will be provided access to the wireless LAN in the POLYMAT when registering on Friday.

## Insurance

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

## Telephone

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The international code for Spain is +34.

## Emergency phone numbers

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Police	092
Firebrigade	112
Ambulance	112

## Taxi numbers

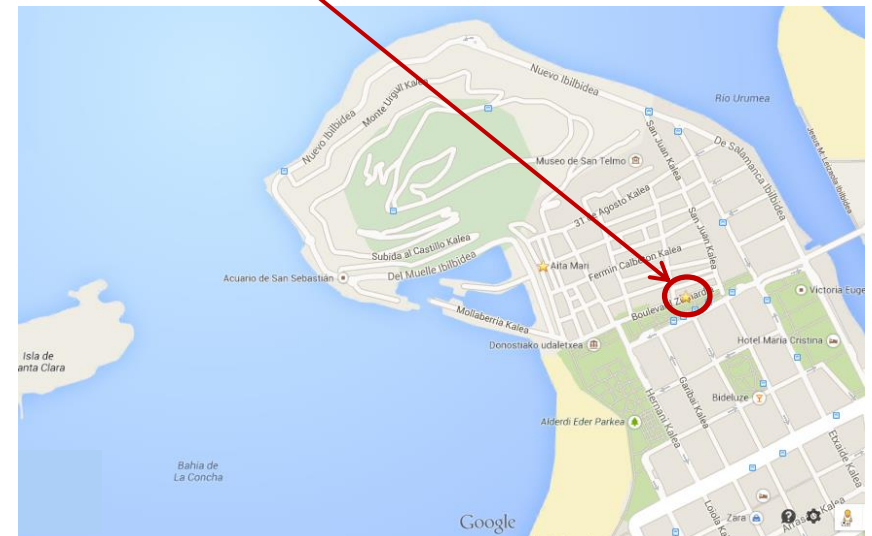
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(+34) 943 46 46 46  
(+34) 943-40 40 40

## Tourist information

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Boulevard, 8 (old town)  
(+34) 943-481 166





# Programme by days

## Friday, 12<sup>th</sup> September 2014



**POLYMAT**



14:00 -14:45 **Registration at the conference site**  
**Poster wall preparation**

14:45 -15:00 **Welcome**  
Prof. Markus Busch, Prof. Jose R. Leiza

### Session I

*Chair: Amaia Agirre (University of the Basque Country, San Sebastián)*

15:00 -15:20 **Paul Aigner** (Johannes-Kepler-University Linz)  
*Influence of Pre-Contacting on the Activity of a Ziegler-Natta Catalyst System*

15:20 -15:40 **Leonhard Mayrhofer** (Johannes-Kepler-University, Linz)  
*Influence of Gas Velocity on the Particle Growth in Gas Phase PE Polymerization*

15:40 -16:00 **Claudia Schwartzkopff** (Technical University Darmstadt)  
*Scanning Transitiometry – A Method to Investigate Phase Transitions and Thermodynamic Properties under High Pressures*

16:00 -17:00 **Coffee Break and Poster Session**

### Session II

*Chair: Joana Kettner (Martin-Luther-University, Halle)*

17:00 -17:20 **Barbara R. Lara** (C2P2 Lyon)  
*Reformulation of Acrylic Latexes for use in Flexible Food Packaging*

17:20 -17:40 **Shaghayegh Hamzehlou** (University of the Basque Country)  
*Simulation of Polyurethan/Acrylic Hybrid Polymerization in Batch Miniemulsion Droplets*



# Programme by days

## Friday, 12<sup>th</sup> September 2014



**POLYMAT**

17:40 -18:00 **Joseba Juaristi** (University of the Basque Country)  
*Morphology and Film Forming Properties of Acrylic Hybrid Emulsions*

18:00 -18:20 **Ana B. López** (University of the Basque Country)  
*Waterborne Fluoropolymer Dispersions for Hydrophobic Coatings*

18:30 -19:00 **Dr. L. Ivano Costa (SULZER)**  
*Process Technology at Sulzer Chemtech: from first concept to guaranteed plant performance*

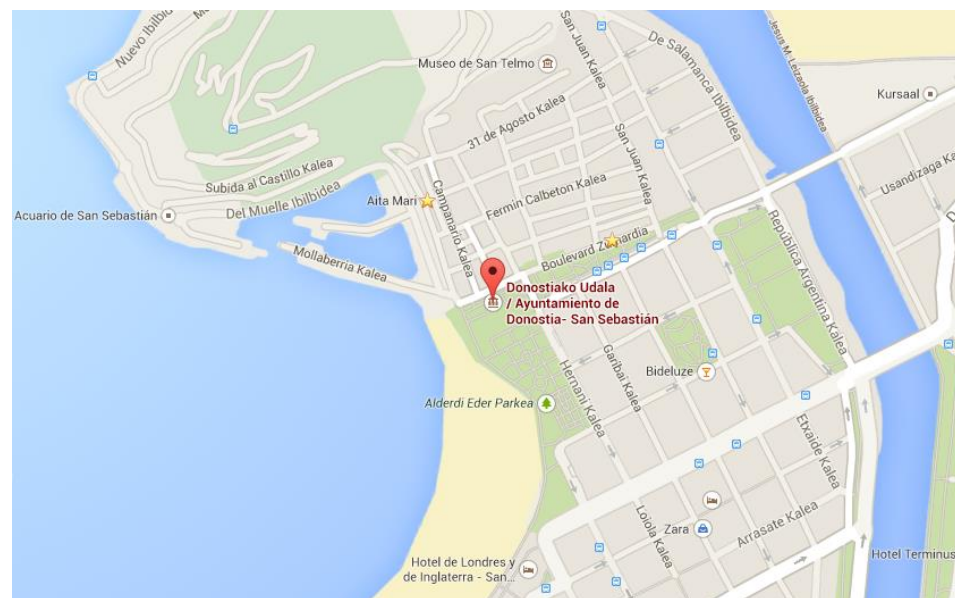
20:00 **Pintxos tour**  
Meeting point: Town hall (ayuntamiento) in the old city of San Sebastián

kindly sponsored by:

**SULZER**

### Pintxos...

literally means „spike“ and is a traditional snack, which is typically eaten in bars in the Basque country.





# Programme by days

## Saturday, 13<sup>th</sup> September 2014



**POLYMAT**

### Session III

Chair: Claudia Schwartzkopff (Technical University Darmstadt)

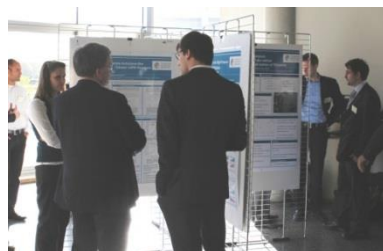
- 09:00 - 09:20 **Ana C. Méndez Ecoscia** (C2P2 Lyon)  
*Colloidal Stability of PVDF Latex Particles*
- 09:20 - 09:40 **Martin Kroupa** (Institute of Chemical Technology Prague)  
*The Discrete Element Model of Shear-Induced Coagulation – the Structure of the Resulting Clusters*
- 09:40 - 10:00 **Barthélémy Brunier** (CNRS-University of Lyon)  
*Analysis of the Effect of Laponite on Radical Exchange in Seeded Semibatch Pickering Emulsion Polymerization*
- 10:00 - 10:20 **Judith van Wijk** (Eindhoven University of Technology)  
*Silica Microcapsules by Templating Pickering Emulsion Droplets: Mechanism of Formation*

10:20 - 11:30

**Coffee Break**

and

**Poster Session**



### Session IV

Chair: Martin Kroupa (Institute of Chemical Technology Prague)

- 11:30 - 11:50 **Leila Medeiros Santos** (C2P2 Lyon)  
*Monitoring of Miniemulsion Polymerization of the Methyl Methacrylate in the Presence of Ionic Liquids using Near Infrared Spectroscopy*
- 11:50 - 12:10 **Sevilay Bilgin** (University of the Basque Country)  
*Stabilization of Emulsions by Using Ionic Monomers*
- 12:10 - 12:40 **Dr. Eric Grolman** (DSM)  
*Working on Polymer Reaction Engineering in DSM's Material Sciences cluster*

13:00

**Lunch at the bar Artikutza, which is in walking distance**  
(Oihenart street, 3)

kindly sponsored by





# Programme by days

## Saturday, 13<sup>th</sup> September 2014



**POLYMAT**

### Session V

*Chair: Andres F. Sierra Salazar (ENSCM, Montpellier)*

- 14:20 - 14:40 **Alejandro Arzac** (University of the Basque Country)  
*Reduced Graphene Oxide/Polymer Composites Latexes by Emulsion and Miniemulsion polymerization*
- 14:40- 15:00 **Alicia De San Luis** (University of the Basque Country)  
*Nanostructured Polymeric Aqueous Dispersions containing Quantum Dots*
- 15:00- 15:20 **Gordana Siljanovska Petreska** (University of the Basque Country)  
*SERS Active Substrates based on Ag/Graphene/Polymer obtained by Laser Ablation using Rh6G as a Model Compound*
- 15:20 - 15:40 **Aintzane Pikabea** (University of the Basque Country)  
*Dual Stimuli-Responsive Nanogels: Promising Nanocarriers for Controlled Drug Delivery*

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

- 16:30-17:00 **Dr. Wolfgang Gerlinger (BASF)**  
*Polymer Reaction Engineering in BASF*

### Session VI

*Chair: Barbara Rezende Lara (C2P2, Lyon)*

- 17:00 - 17:20 **Pavel Ferkl** (Institute of Chemical Technology Prague)  
*Heat transfer Phenomena in Micro- and Nanocellular Foams*
- 17:20- 17:40 **Joana Kettner** (Martin-Luther-University, Halle)  
*Kinetic Study of the Bulk Polymerization of Propylene with Metallocene Catalyst using Reaction Calorimetry*
- 17:40 - 18:00 **Arkom Drawpateep** (Martin-Luther-University, Halle)  
*High Impact Polypropylene Process Review and Future Trend in Research*
- 18:00 - 18:20 **Miguel Plata** (Martin-Luther-University, Halle)  
*Experimental Setup for Heterophasic Propylene Copolymers*

18:20-19:00 **Refreshments and Poster Session**





# Programme by days

## Saturday, 13<sup>th</sup> + Sunday, 14<sup>th</sup>



### POLYMAT

20:30

**Dinner at the restaurant Aita Mari**  
(Puerto street, 23)

kindly sponsored by



*Sunday, 14<sup>th</sup>*

11:00 **Guided tour through the old town of San Sebastián**

Meeting point: Town hall (ayuntamiento) in the old city  
of San Sebastián



13:30 **Lunch at the hotel Eceiza with the award for the best contribution**

Satrustegi street, 13  
(Ondarreta beach)

Lunch & tour kindly sponsored by



The prize for the best contribution  
is kindly sponsored by

### WILEY



# Places to know



**POLYMAT**

## POLYMAT Institute



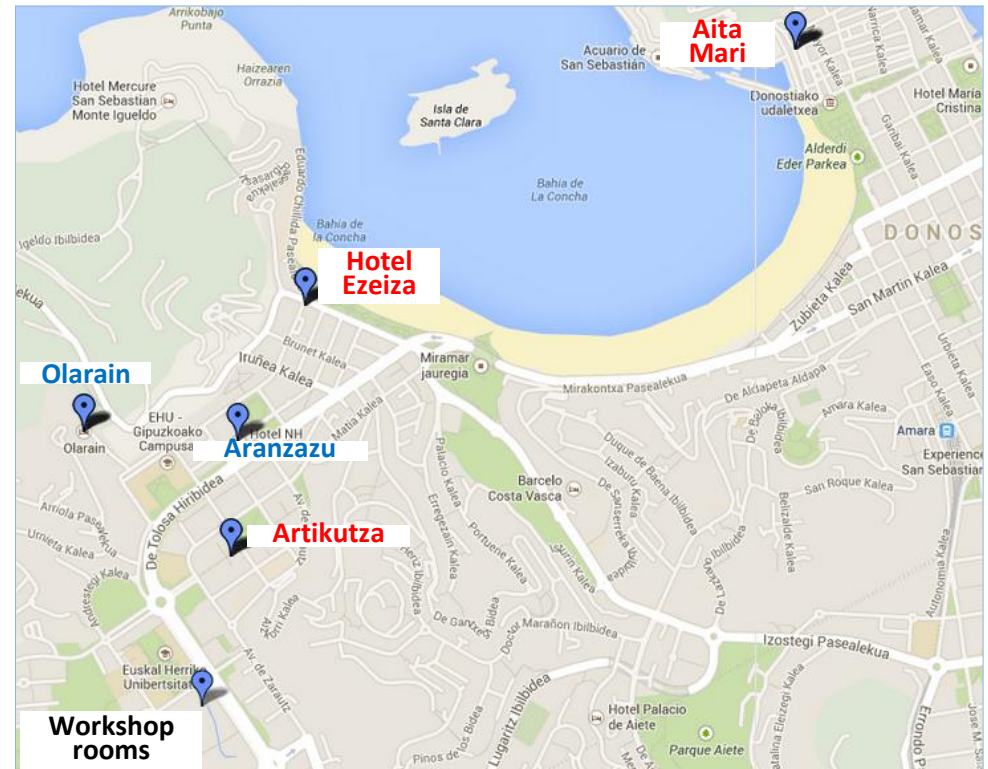
**Joxe Mari Korta  
Center**

Avda. Tolosa, 72  
20018 Donostia  
- San Sebastian  
SPAIN



## San Sebastián Overview

- Hotels
- Restaurants
- Workshop rooms





# List of posters

- P. Ferkl, R. Pokorny, J. Kosek**  
Polymeric Foams: Morphology and Heat Transfer
- A. Gapchenko, H.-U. Moritz, W. Pauer**  
High-Temperature Emulsion Polymerization of Styrene and n-Butyl Acrylate
- M. Balyschewa, M. Busch**  
Cloud Point Pressure Curves of High Density Ethylene Acrylate Copolymers
- A.B.López, J.C. de la Cal, J.M. Asua**  
Waterborne Fluoropolymer Dispersions for Hydrophobic Coatings
- J. Juaristi, P.-E. Dufils, A. Veneroni, Y. Vanderveken, J. M. Asua**  
Morphology and Film Forming Properties of Acrylic Hybrid Coatings
- B. Brunier**  
Evaluation of Laponite Partitioning in Pickering Emulsion Polymerization
- A. C. Méndez-Ecoscia, M. Fonseca-Marques, T.F.L McKenna, N. Othman**  
Colloidal Stability of PVDF Latex Particles
- L. Medeiros Santos, M. J. Amaral, M. Fortuny, C. Dariva, E. Franceschi, A. F. Santos, T. F.L. McKenna**  
Monitoring of Miniemulsion Polymerization of the Methyl Methacrylate in the Presence of Ionic Liquids using Near Infrared Spectroscopy
- A. Pikabea, J. Ramos, J. Forcada**  
PH- and T-responsive nanogels: potentially useful vehicles in controlled drug release
- M. Madani, H.- U. Moritz, W. Pauer**  
Fouling in a Batch Reactor during an Emulsion Polymerization
- N. Monien, W. Pauer, H.-U. Moritz, C. Scholten, E. Alsaffar**  
Swelling Capability of Hydrophilically Modified Polyurethane Polymers
- K. Rossow, F. G. Lueth, W. Pauer, H.-U. Moritz**  
Process Intensification through Smart Scale Technology in Continuous Emulsion Polymerization
- P.Aigner, C. Paulik, A. Krallis**  
Influence of Pre-Contacting on the Activity of a Ziegler Natta Catalyst in a 0.5 L Polymerization System
- A. Drawpateep, T. Kroener, M. Bartke**  
Kinetics of Copolymerization of Acrylamide and MADAMBQ



# List of posters

15. **C. W. Nörnberg, B. Schroeter, W. Pauer, H.-U. Moritz, W.-D. Hergeth**  
Continuous Emulsion Copolymerization of Vinyl Acetate in a Laminar Stirred Tube Reactor (LSTR)
16. **M. Kroupa, M. Vonka, J. Kosek**  
Shear-induced Coagulation in Colloidal Dispersions - Modeling by Discrete Element Method
17. **B. R. Lara, T.F.L. McKenna, K. Ouzineb**  
Reformulation of Acrylic Latexes for use in Flexible Food Packaging
18. **A. De San Luis, A. Bonnefond, M. Paulis, J.R. Leiza**  
Nanostructured polymeric aqueous dispersions containing quantum dots
19. **M. Öppling, M. Busch**  
Influence of RAFT-Agents on the Radical High Pressure and High Temperature Ethylene Polymerization
20. **Leonhard Mayrhofer**  
Single particle gas-phase ethylene homo-polymerization with Ziegler-Natta catalyst



# Abstracts of all participants



**POLYMAT**

1. Paul Aigner
2. Leonhard Mayrhofer
3. Claudia Schwartzkopff
4. Bárbara Rezende Lara
5. Shaghayegh Hamzehlou
6. Joseba Juaristi
7. Ana Belén López González
8. Ana Carolina Méndez-Ecoscia
9. Martin Kroupa
10. Barthélémy Brunier
11. Judith van Wijk
12. Leila Medeiros Santos
13. Sevilay Bilgin
14. Alejandro Arzac
15. Alicia De San Luis
16. Gordana Siljanovska Petreska
17. Aintzane Pikabea
18. Pavel Ferkl
19. Joana Kettner
20. Arkom Drawpateep
21. Miguel Plata
22. Mania Madani
23. Nicole Monien
24. Kristina Rossow
25. Christian Werner Nörnberg
26. Margarita Balyschewa
27. Alisa Gapchenko
28. Maria Öppling

## Influence of Pre-Contacting on the Activity of a Ziegler-Natta Catalyst System

Paul Aigner, Institute for Chemical Technology of Organic Materials (CTO), Johannes Kepler University, Austria;

C. Paulik, Institute for Chemical Technology of Organic Materials (CTO), Johannes Kepler University, Austria;

A. Krallis, Borealis Polymers Oy, Finland

### INTRODUCTION

Polyolefines account for about one third of the Plastics production [1]. For the production of Polyolefines heterogeneous Ziegler-Natta based catalysts dominate the market. There is a constant progress in catalyst design to increase the catalyst activity [2]. To reach the maximum potential of a catalyst system several steps prior the main polymerization process need to be done. It has been shown that pre-polymerization and pre-contacting can increase the activity of catalyst system dramatically [3,4]. The catalyst system usually consists out of a TiCl<sub>4</sub> based component and an aluminium-alkyl. Out of these two components an active center as shown in Figure 1 is formed, which is required to perform the polymerization process. The formation of the active center has a big influence on the catalyst productivity.

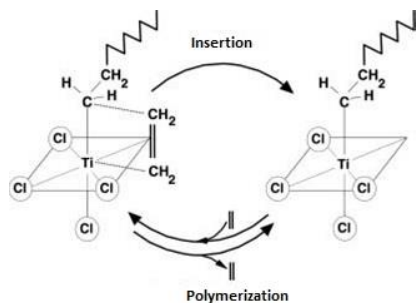


Figure 1: Active center and polymerization scheme [5].

### PRACTICAL PROCEDURE

Therefore a more detailed investigation has been performed to study the relation between activity and pre-contacting of a Ziegler-Natta catalyst system for polyethylene. In addition the polymer powder properties such as crystallinity, molecular weight and particle morphology have been analyzed as well. The experiments have been performed in 0.5 l multi-purpose reactor system in slurry. Triethylaluminium (TEA) has been used as co-catalyst. Of special interest has been the influence of the pre-contacting duration on the catalyst activity. For that reason the pre-contacting time has been varied. The polymerization time has been one hour at 85 °C. Furthermore the catalyst behavior when copolymerizing ethylene with other  $\alpha$ -olefins has been looked at.

### RESULTS

The investigation reveals an optimum pre-contacting time. There is a linear increase of the activity till the maximum and afterwards it decreases again. At the optimum pre-contacting the activity increases by 25 % compared without pre-contacting. Beyond the optimal pre-contacting time it nearly decreases to the starting value again. The activation via pre-contacting is heavily dependent on the catalyst and the conditions, but with just the right timing, pre-contacting can increase the productivity by one quarter.

### REFERENCES

- 1) PlasticsEurope, (2013), Plastics - The Facts 2013, <http://www.plasticseurope.org/cust/documentrequest.aspx?DocID=59108>, accessed on: 2/7/2014.
- 2) Galli P., Vecellio G., Technology: driving force behind innovation and growth of polyolefins, *Progress in Polymer Science*, (2001), 26(8), 1287–1336.
- 3) Daftaribesheli M., Comparison of catalytic ethylene polymerization in slurry and gas phase, (2009), University of Twente [Host], Enschede.
- 4) McKenna, Timothy F. L., Tioni E., Ranieri M. M., Alizadeh A., Boisson C., Monteil V., Catalytic olefin polymerisation at short times: Studies using specially adapted reactors, *Can. J. Chem. Eng.*, (2013), 91(4), 669–686.
- 5) Böhm L. L., The ethylene polymerization with Ziegler catalysts: fifty years after the discovery, *Angew. Chem. Int. Ed. Engl.*, (2003), 42(41), 5010–5030.

### Your notes:

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## Scanning Transitiometry – A Method to Investigate Phase Transitions and Thermodynamic Properties under High Pressure

*Claudia Schwartzkopff, Technische Universität Darmstadt, Ernst-Berl-Institut für Technische und Makromolekulare Chemie, Germany;  
M. Busch, Technische Universität Darmstadt, Ernst-Berl-Institut für Technische und Makromolekulare Chemie, Germany*

Nowadays heat integration is a crucial task in the development and optimization of chemical processes and contributes non-negligibly to their profitability. However, before dealing with the energy efficiency of a system, information on the thermodynamic properties of the involved substances at process conditions is needed. In most cases reliable data sets including miscibilities and the associated enthalpies of mixing as well as heat capacities for the main components are already available from different databases. Elsewise those quantities can be measured in a straightforward manner by means of standard analytical techniques, which have been approved for ambient and low pressures.

In the field of polyolefines the measurement of thermodynamic properties is in fact more delicate since one may encounter process pressures of up to 3000 bar such as in the LDPE production. Moreover these high pressures are accompanied by high temperatures of 200-300 °C. Such extreme conditions complicate the determination of thermodynamic data because of the conflicting requirements of high sensitivities on the one hand and pressure-tight design of the sample vessels on the other hand. In order to overcome this contradiction several concepts have been developed.

One idea for the investigation of polymer miscibility with low molecular fluids under high pressures and temperatures is the use of autoclaves with a transparent sapphire window, so called visual cells. With the latter cloud points are determined by visual observation of the polymer precipitation. However, the results of these measurements can vary depending on the operator and the derivation of reliable quantitative information on solubility is difficult if not impossible. [1]

In comparison to the visual cell scanning transitiometry represents a more sophisticated method to examine miscibilities and other thermodynamic properties under high pressures. [2] This rather unknown technique is introduced and its advantages are discussed. The calibration procedure is outlined and the reproducibility of the measurements reviewed. The first experiments employing scanning transitiometry in our group are presented showing the effects pressurizing media on melting and crystallization of a low density PE polymer under ambient to medium pressures. An outlook on future applications of scanning transitiometry for the determination of enthalpies of mixing and heat capacities under high pressures up to 2500 bar is given.

## REFERENCES

- 1) R. Dohrn, J.M.S. Fonseca, S. Peper, Experimental methods for phase equilibria at high pressures, *Annual Review of Chemical and Biomolecular Engineering*, 3, 343, 2012.
- 2) S. L. Randzio, Ch. Stachowiak, J.-P.-E. Grolier, Transitiometric determination of the three-phase curve in asymmetric binary systems, *J. Chem. Thermodyn.*, 35, 639, 2003.

## Acknowledgments:

Claudia Schwartzkopff gratefully acknowledges her scholarship funded by the Merck'sche Gesellschaft für Kunst und Wissenschaft.

## Your notes:

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## Morphology and Film Forming Properties of Acrylic Hybrid Emulsions

*Joseba Juaristi, J. M. Asua*

POLYMAT, University of the Basque Country UPV/EHU, 20018 Donostia-San Sebastián, Spain

Waterborne coatings have attracted a lot of interest in the last years, as a sustainable alternative to the use of solvent based coatings. The advantages in the use of such a kind of product are to be found in the limitation in the use of VOCs (volatile organic compounds) and in the possibility of application at room temperature. These coatings can also reduce the amount of hazardous waste generated, depending on the type of paint used. Waterborne coatings may benefit from the presence of domains with either high T<sub>g</sub> or crystallinity.<sup>1,2</sup> These coatings often present resistance to different agents and/or good barrier properties.<sup>3</sup> In order to optimize the properties an adequate balance between the hard polymer and the soft film-forming polymer should be achieved. A possibility is a blend of dispersion of hard polymer and acrylic resins using seeded emulsion copolymerization.<sup>4</sup> However, phase separation often occurs upon film formation leading to poor application properties. Incorporation of both hard and soft phases in the same particle would minimize this effect. In the implementation of this idea there are plenty of open questions regarding aspects as particle morphology, fractions of soft and hard phases and degree of interpenetration among the phases.

This work is an attempt to clarify some of these open questions. In particular, using a core-shell morphology with the soft polymer in the shell, which was considered to be the most promising morphology, the effect of the fractions of soft and hard phases and degree of interpenetration among the phases on film formation was investigated.

The core-shell particles were synthesized in a two-step process. In the first step, a densely crosslinked particle was formed by semicontinuous emulsion copolymerization of styrene and divinylbenzene. The shell was formed in a seeded semicontinuous emulsion copolymerization process, using the particles produced in the first stage as a seed. The composition of the shell was varied and copolymers of styrene/butyl acrylate and methyl methacrylate/butyl acrylate were used. The composition of the shell was adjusted to have a low enough T<sub>g</sub>. In some cases a super-spreader was added to facilitate film formation of solids surfaces by decreasing the surface tension of the latex.

The results in Table 1 show that the fraction of soft copolymer has a strong effect on film properties. Taking into account that the maximum volume fraction for monodispersed packed spheres is 64%, one would expect to have continuous film of soft polymer for shell contents in the range of 36-40%. However, Table 1 shows that a substantially higher fraction is needed to achieve the MFFT characteristic of the polymer in the shell. This strongly suggests that there is some interpenetration between the soft shell and the hard core that resulted in a lower fraction of soft shell useful to form film.

Shell (%)	22	27	36	45	55	65
MFFT (°C)	>90	>90	85	58	21	13

Table 1: Values of minimum film formation temperature (MFFT) for p(St/DVB)/p(MMA/BA) systems.

TEM analysis of the samples reveals that the particles had a core-shell morphology and the acrylic rich copolymer (clear polymer in the TEM picture) was mainly located in the shell. However, the thickness of the shell is too thick for the fraction of the copolymer used. This further supports the idea that there is a penetration of the soft polymer in the core.

The research reveals that the incorporation of small amounts of low-T<sub>g</sub> polymer into a high-T<sub>g</sub> crosslinked core can substantially improve the film forming properties of the coatings. However, penetration of the low T<sub>g</sub> polymer in the core needs to be avoided in order to optimize the amount of acrylic polymer in the formulation.

### REFERENCES

- 1) Patent No. 5,783,632
- 2) Patent No. 5,612,415
- 3) F. Bückman, A. Overbeek, T. Nabuurs, (2001). Self Crosslinking Surfactant Free Acrylic Dispersions for High Performance Coatings Applications. *European Coatings Journal*, 53, pp.1-8
- 4) Helmiyati, Budianto, E. (2008). Emulsion Polymers of Core-Shell Styrene-Butyl Acrylate: The Effect of Feeding and Aging Time on Particle Size Distribution. *Journal of Physical Science*, 19(2). pp. 117-125

### Your notes:

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

*Barthélémy Brunier, Y. Chevalier, N. Sheibat-Othman, LAGEP / CNRS-University of Lyon, France  
E. Bourgeat-Lami, C2P2, LCPP group / CNRS-University of Lyon, France*

"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<sup>[1]</sup> and is named "Emulsion polymerization" by analogy to solid-stabilized emulsions<sup>[2]</sup>. 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<sup>[3]</sup>.

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:

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

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"  $F_p$ :

$$k_c^p = 4\pi \cdot r_p \cdot D_w \cdot \bar{F}_p$$

Hansen and Ugelstad [7] also proposed an equation that combines the electrostatic repulsion factor, with capture reversibility to obtain the expression of  $F_p$ . 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.

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## Kinetic Study of the Bulk Polymerization of Propylene with Metallocene Catalyst using Reaction Calorimetry

*Joana Kettner, M. Bartke, Martin-Luther-University Halle-Wittenberg, Institute for Chemistry, Polymer Reaction Engineering, Germany;  
M. Dietrich, T. Sell, Lummus Novolen Technology GmbH, Germany*

In comparison to the gas-phase or slurry polymerization, the kinetics of the polymerizations carried out in bulk phase are more difficult to investigate. In gas-phase or slurry processes, kinetic information are accessible by semi-batch operation of the reactor: In batch operation with increasing conversion, the pressure would drop; in semi-batch operation this pressure drop is compensated by feeding of monomer controlled by a pressure control loop. As long as isothermal conditions are met and external mass-transfer restrictions are avoided, the fed amount of monomer corresponds to the monomer consumption and is proportional to reaction rate.

In case of the bulk polymerization, the reactor pressure in principle always corresponds to the vapor pressure of liquid propylene, which is constant with conversion. The semi-batch approach outlined above is therefore not applicable. Furthermore, the monomer concentration in the reactor is higher leading to higher polymerization rates compared to slurry- or gas-phase polymerization.

In literature, only a few references about online-measurement of bulk phase polymerization can be found using either reaction calorimetry<sup>1,2,3</sup> or dilatometry<sup>4,5</sup>.

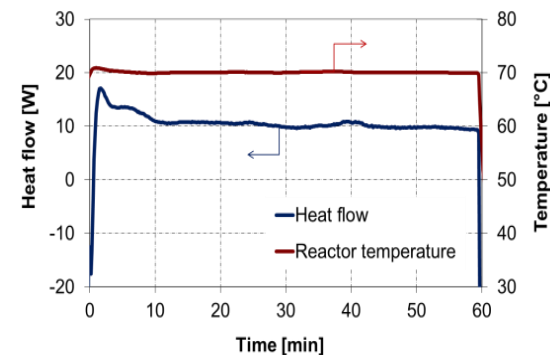
In this study a reaction calorimeter from ChemiSens® was used, which is based on the principle of the heat flow calorimetry. The main advantage of this special calorimeter is that the heat flow can be measured independent of the heat transfer conditions and filling level in the reactor. The heat flow is measured via the heat conductivity in the reactor base. No calibration is needed.

The reaction kinetics can be directly determined from the generated chemical heat of the reaction, because it is direct proportional to the reaction rate. The heat input of the stirrer is measured by means of a torque transducer.

The purpose of the study is the kinetic investigation of the bulk phase polymerization of propylene with a supported metallocene catalyst. Main approach is to investigate the influence of different reaction conditions (reaction temperature, hydrogen concentration) on activity and to determine the kinetics of the catalyst.

Two different polymerization procedures were investigated: polymerization with non-isothermal prepolymerization and polymerization with prepolymerized catalyst. In the first procedure, the prepolymerization starts with the injection of the catalyst at mild conditions. During the prepolymerization, the reactor temperature is increased until the desired reaction

reached and the main polymerization starts. In the second procedure, the prepolymerized catalyst is firstly produced at milder reaction conditions and stored under inert conditions. In the main polymerization, the prepolymerized catalyst is directly injected under reaction conditions.



$$\rightarrow \dot{Q}_{Chem} = rate \cdot (-\Delta H_R) = \dot{Q}_{HF} - P_{stirr}$$

The results from polymerizations carried out at same reaction conditions show that the reached activities are comparable for both processes. Nevertheless, the main advantages of the second procedure are: no undefined heating up-periods during prepolymerization, degree of prepolymerization is known, kinetic profiles are earlier accessible because isothermal conditions are reached faster.

The presented study therefore focuses on the polymerization with prepolymerized catalyst. The influences of reaction temperature in the main polymerization and the amount of hydrogen on the activity are investigated. Furthermore, prepolymers with different degree of polymerization were prepared in order to investigate the influence of DP on activity in the main polymerization process.

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### Your notes:



## High Impact Polypropylene Process Review and Future Trend in Research

*Arkam Drawpateep, Martin Luther University, Germany;  
M. Bartke, Martin Luther University, Germany*

Having versatile properties and wide range of applications, plastic plays a vital role in our daily life. In 2012, 288 tons of plastic has been produced around the world. One among the most pronounced plastic regarding its consumption is polypropylene (18.8%). After the first discovery of isotactic polypropylene by G. Natta et al. in 1954, polypropylene has shown a significantly improvement in term of product properties. One major direction in polypropylene development is to extend its application at low temperature, since isotactic polypropylene glass transition temperature ( $T_g$ ) is around 0°C. In order to extend polypropylene application in sub-zero temperature environment, the so called high impact polypropylene was developed.

The high impact polypropylene consists of isotactic polypropylene matrix and finely dispersed elastomeric phase. Originally achieve by compounding isotactic polypropylene and elastomeric material likes ethylene-propylene rubbers (EPR) or ethylene-propylene diene elastomers (EPDM). Later on the catalyst development and process technology improvement had driven the production of high impact polypropylene to in-reactor design. The driving force was not only energy saving by elimination of compounding step, but the resin produced in reactor offers better particles morphology and performance.

Nowadays, production of high impact polypropylene is achieved by using two stages in series process. In the first stage, isotactic polypropylene continuous phase matrix is produced in liquid or gas phase process. In the second stage, elastomeric phase of ethylene-propylene copolymer is formed into the former isotactic polypropylene particle to enhance homogeneously dispersion of elastomeric phase. Number of industrial process were developed and used to produce high impact polypropylene including Spheripol, Spherizone, Catalloy process (Lyondell Basell), Borstar (Borealis), Unipol process (Dow Chemicals), Hypol II (Mitsui Chemicals), Novolen process (Lumus Novolen Technology), Amoco process (Ineos), vertical stirred-bed gas phase process (BASF).

The process most widely used for commercial PP production is the Spheripol process by Lyondell Basell. Lyondell Basell claims that the process has over 100 licensed lines around the world, with more than 20 million tones capacity. Spheripol is a hybrid process consists of two loop reactors and fluidized bed reactor connected in series. The homopolymerization to form isotactic polypropylene continuous phase matrix is conducted in the bulk phase loop reactors. The typical operating conditions in bulk polymerization are 50 - 80°C, 20 – 40 bar. The benefits of using this loop reactor cascade are: high specific cooling surface, excellent heat and mass transfer condition, narrow residence time distribution, full use of reactor volume, and less investment cost. It has been widely regards as the most important technology to produce homopolypropylene.

In the second stage, elastomer phase is produced in gas phase fluidized bed reactor. The heterophasic copolymer with up to 25 wt% ethylene content is formed. This copolymerization step is performed in gas phase polymerization, to avoid dissolution of the amorphous copolymer in liquid propylene. The general operating conditions in gas phase polymerization are 50 - 80°C, and 10 – 20 bar.

The research and development in high impact polypropylene is continuing in all areas including production process, catalyst and product development. In term of product, the challenges are on improving stiffness, toughness, transparency, and processability. Incorporating more than one disperse phase to enhance toughness of the product is also being interests. The catalyst development is moving toward single site catalyst, while development in Ziegler-Natta catalyst is still focus on the support size, internal and external donors and control of the different kind of active sites. The concept of hybrid catalyst system could also be an option for producing wider range of high impact polypropylene. Regarding legal regulation the development phthalate free catalyst system will soon become essential. In process development, recently multi-zone circulating reactor received highly interests. The continuous multi-stage polymerization offers short residence time for particle to circulate between two phase of polymerization, resulting highly uniform copolymer component dispersion.

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**Experimental Setups for Heterophasic Propylene Copolymers.**

*Miguel Plata, Martin Luther University, Germany*

Heterophasic propylene copolymers (Hecos's) are versatile polymeric materials used in various applications, for instance in the automotive industry. Heterophasic propylene copolymers consist of a polymer matrix of isotactic polypropylene homopolymer and a dispersed rubbery ethylene-propylene copolymer not miscible with the matrix phase. While the matrix gives good stiffness, the elastomeric phase improves impact strength and low temperature behavior.

Heterophasic propylene copolymers are produced by coordinative polymerization in at least two-stage processes. For heco-PP, commercially predominantly Ziegler-Natta catalysts are used. While the matrix material is either produced in gas-phase or bulk polymerization, the elastomeric phase is produced in all commercial processes by gas-phase polymerization.

For product development, rubber content, rubber distribution and molecular structure of both matrix material and elastomeric material have to be precisely controlled. In coordinative polymerization, the polymerization kinetics depends strongly on the used catalyst system and the polymerization conditions applied. Since there is a continuous development of both new catalysts systems and polymer products, there is a constant need for experimental kinetic data of new polymerization catalysts and for producing polymer samples for establishing of structure-property relationships.

In the contribution, two reactor setups for heterophasic polypropylene polymerization will be presented. One setup for gas-phase polymerization of both matrix and heco-material already exists and has been broadly used already, another setup for bulk-polymerization of the matrix material and subsequent gas-phase polymerization of the elastomeric material is currently build up. Both setups consist of five-liter-reactors, enabling to produce up to 700 g of material per run, which is enough in order to perform mechanical material tests. While the bulk polymerization is done in batch mode, the gas-phase polymerizations are carried out in semi-batch mode and both monomer consumption and gas composition can be monitored. The gained data can be used for development of kinetic models for further product- and process development.

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## Fouling in a Batch Reactor During an Emulsion Polymerization

*Mania Madani, H.- U. Moritz, W. Pauer*

Fouling is the general name for the pollution and coating on the walls of chemical reactors. The goal of the work is to extend the understanding and to quantify the influencing parameters for fouling formation during an emulsion polymerization.

Regarding the surface properties it is known that free surface energy and roughness are main parameters responsible for fouling formation. Additionally to these, the testing surfaces were analyzed in more details to gain information about the correlation between the surface properties and the degree of fouling. In that context, the free surface energy, the hysteresis and the wettability by emulsions were determined.

In order to quantify the influencing parameters for fouling formation the amount of fouling was gravimetrically determined on different surfaces. For that purpose, the testing surfaces were fixated within the batch reactor before the emulsion polymerization was started.

The free surface energy was determined by the method of sessile drop. With this method the contact angle between a liquid and the testing surface is measured. The contact angle is defined by the shape of the drop on the three phase contact line between solid, liquid and vapor. This measurement was done with two different liquids on each testing surface. The free surface energy was calculated by the Young-Laplace equation.

The hysteresis of the testing surfaces was determined by using the advancing- receding method. To a drop on a surface a defined amount of liquid is added or removed, while the contact line is pinned. By adding the liquid the contact angle increases (advancing) and by removing the liquid the contact angle recedes (receding). The hysteresis of the regarded surface is the difference between these two measured contact angles.

In order to determine the wettability of the testing surface an emulsion was dosed onto the surface and the contact angle was measured. The smaller the measured contact angle is the better is the wettability of the testing surface. Contact angles larger than 90° correspond to a bad wettability.

Comparing the amount of fouling on the surfaces with the surface properties it was observed that the surfaces with higher surface energy lead to more fouling. Also, the wettability showed an influence on the fouling behavior: the better the wettability the more fouling is formed. The hysteresis provides information about the degree of the roughness of the surface.

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**Swelling Capability of Hydrophilically Modified Polyurethane Polymers**

*Nicole Monien, W. Pauer, H.-U. Moritz, Universität Hamburg, Hamburg, Germany;  
C. Scholten, Synthomer Deutschland GmbH, Marl, Germany;  
E. Alsaffar, Synthomer Harlow, United Kingdom*

Polyurethanes are known for their superior mechanical properties and high resistance against solvents. Nowadays there is an increasing use of aqueous polyurethane dispersions (PUD). These dispersions offer the advantage of a low content of volatile organic compounds. However there is a serious drawback of PUDs. The production cost of these PUDs is much more expensive in comparison to aqueous acrylic dispersions. Therefore it is of interest to develop a system which combines the excellence of PUDs while retaining the low production costs of the acrylic dispersions. These aqueous polyurethane acrylic hybrid dispersions can be synthesized by different routes. One possibility is the preparation of blends of PUDs and acrylic dispersion. A severe disadvantage of these dispersion blends are the poor mechanical properties. Another possibility is the preparation by miniemulsion polymerization which offers better results, but exhibits scale up problems. An alternative to these synthesis routes is the possibility to polymerize acrylate in presence of PUDs. These PUDs are prepared from hydrophilically modified Polyurethane polymers (PU polymers). The PU polymers are polymerised using a hydrophilic monomer, long chain diols and isocyanates.

An important property of the modified PU polymer is the swelling ability. Hydrophobic monomers can swell the hydrophilically modified PU polymers and are stabilized by the PU polymer. Higher degrees of swelling allows for more incorporated acrylic monomers after polymerization.

Therefore the swelling behavior of different acrylates in PU polymers has been analyzed. The extent of swelling was determined by analyzing the remaining monomers with gas chromatography. The particle size of the monomer swollen PU polymers and the polymerized polyurethane acrylic hybrid dispersion has been measured by dynamic light scattering (DLS).

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*Kristina Rossow, F. G. Lueth, W. Pauer, H.-U. Moritz, University of Hamburg, Germany*

The high specific surface area of a milli-sized tube reactor (length: 10 m, inner diameter: 10 mm, production volume in range of kg/h) provides certain benefits in matters of heat-transfer, inherent process safety and therefor offers a high potential in process intensification.<sup>1</sup> By means of a case study the characteristics of an emulsion copolymerization in a milli-sized tube reactor are presented in terms of e.g. conversion slopes, molecular weight distribution and particle sizes. The impact of process parameter variation such as the molar ratio of the monomers, the monomer/water ratio and different operation modes are shown. Besides the poster shows the experimental set-up and gives an overview of the reactor properties.

Using PTFE as reactor material offers a lot of advantages referring to surface fouling<sup>1</sup> and flexibility in reactor design. The helical coiled reactor geometry, leading to secondary flow phenomena<sup>2</sup> like dean vortices, in combination with integrated static mixing elements<sup>3</sup> results in narrowed residence time distribution and improved heat transfer properties.<sup>1</sup> The combination of reactor geometry and material 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. Besides the used reactor set-up and the case study emulsion show a good stability towards temperature disturbances in the inlet as well as in the jacket temperature of more than 15 °C. This robustness of the system towards external disturbances allows a wide application range by means of online feedback control.

In order to get information about the progress of the reaction the experimental set-up is designed to allow sampling at various residence times without influencing the mass flow, thus the flow properties and the final product. That way a lot of reaction properties as the total conversion, the particle size, temperature can be gained by a single experiment for different reaction states.

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## Cloud Point Pressure Curves of High Density Ethylene-Acrylate Copolymers

*Margarita Balyschewa, Technische Universität Darmstadt, Ernst-Berl-Institut für Technische und Makromolekulare Chemie, Germany;*

*M. Busch, Technische Universität Darmstadt, Ernst-Berl-Institut für Technische und Makromolekulare Chemie, Germany*

During the high pressure polymerization process of polyethylene and polyethylene copolymers it must be ensured that polymerization takes place in homogeneous single phase, to obtain a uniform product of high quality. Therefore, a good knowledge of phase behavior of the reaction mixture is crucial. Measuring of cloud-point curves provides a facile method to determine the boundary between single and two-phase area.

Copolymerization represents an effective way to modify polymer properties. Even small incorporation ratio of comonomer cause great changes. Copolymerization of ethylene with polar comonomers occurs present by free-radical polymerization. The resulting copolymer consists of short- and long-chain branches. Catalytic polymerization offers a way to achieve linear microstructured polyethylene. However copolymers with polar comonomers, by using common industrially catalyst, like Ziegler-Natta and Metallocens, cannot be achieved. Such catalyst based on early transition metals which show high oxophilicity. Thereof results strong bonds between metal and polar group.

Novel late transition metal catalyst with general formula (NiPh(P,O)) are less oxophilic, which allows the copolymerization of ethylene with polar comonomers. In our working group we investigate the influence of high pressure and temperature (up to 2000 bar and 200°C) on the copolymerization behavior of such catalysts which are also known as SHOP-type-catalysts (Shell Higher Olefin Process).

In this work cloud-point curves of high-density ethylene-methyl acrylate and ethylene-n-butyl acrylate copolymers in supercritical ethylene and accordingly comonomer as solvent have been measured. The measurements are carried out in an optical high pressure view cell with moving piston up to 2000 bar and 260°C. The influence of different comonomer incorporation ratio on the cloud point pressure point was examined.

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**High-Temperature Emulsion Polymerization of Styrene and N-Butyl Acrylate**

*Alisa Gapchenko, H.-U. Moritz, W. Pauer, University of Hamburg, Germany*

This work focusses on several aspects regarding the emulsion copolymerization of styrene and butyl acrylate at elevated temperatures. Processes with reaction temperatures above 70°C have not been sufficiently investigated yet; the particular interest of this work concentrates on batch reactions in the range of 70°C up to 180°C. An increase of temperature results not only in an increase in the polymerization rate but also in background polymerization processes (such as backbiting,  $\beta$ -scission, thermally initiated polymerization, etc.). Those processes along with the reaching of the ceiling-temperature can be crucial in the mechanism of polymerization and may eventually replace the use of initiators.

All the styrene butyl acrylate emulsion polymerization experiments were carried out in an automated reaction calorimeter at a starting pressure of 2 bar and nitrogen atmosphere. The solids content was 11 wt% with the styrene/butyl acrylate ratio of 50/50 mol% for each selected reaction temperature. The mechanism of the polymerization was examined through the obtained calorimetric data, the molar mass and particle size distributions, the conversion of monomers and NMR.

Up to 110°C a rate maximum was reached at a similar conversion, implying the simultaneous beginning of the Interval III (disappearance of monomer droplets), however the constant rate period (Interval II) disappeared due to the combination of nucleation and propagation reactions. At higher temperatures the amount of self-initiated processes increases, at 180°C no differences in conversion of thermally and radically initiated reactions was observed. An increase of the polydispersity index as well as particle size was observed for reaction temperatures higher than 110°C. An extended comparison with literature data shows the need of review of the classic emulsion polymerisation mechanism for high temperature processes.

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## Influence of various Agents on the Radical High Pressure and High Temperature Ethylene Polymerization

*Maria Öppling, Technische Universität Darmstadt, Ernst-Berl-Institut für Technische und Makromolekulare Chemie, Germany;*

*M. Busch, Technische Universität Darmstadt, Ernst-Berl-Institut für Technische und Makromolekulare Chemie, Germany*

Although low density polyethylene is a very common and widely used polymer it still poses challenges for reaction engineers. This contribution deals with the structural gap between polyethylene formed by catalytic reactions and free radical ones: Polymer manufactured by catalytic processes is linear and long chain branches are introduced by comonomers. In radical polymerization processes of ethylene the molecular architecture is developed depending on process conditions such as temperature and pressure. However, these reaction parameters can only be varied in a range limited by the need of one-phase-systems and the threshold of ethylene decomposition.

Polymers with a lot of long chain branches, less short chain branches and low PDI cannot be formed by either of the mentioned processes. This contribution deals with additional agents, which are able to interfere in the radical polymerization mechanism and could possibly lead to such tailor made polymers. Methods and experimental set-ups to determine the influence of those substances have been tested.

Before testing the agents in polymerization systems they have to be checked with regard to their stability in ethylene up to 2000 bar and 330 °C. A high pressure differential thermal analysis (HP-DTA) setup is used for this examination. In addition, the phase behavior of the substances is analyzed in a high pressure viewing cell. To ensure an invariable composition during the experiment containing temperature and pressure scans the inner volume of the cell is adjusted by a moveable seal.

The final polymerization experiments are conducted in a stirred high pressure batch reactor with injection system for initiator and additional substances. All experiments have an initial pressure of 2000 bar whereas the start temperature is modified between 160-170°C and the duration of an experiment varies between 1 minute and 24 hours.

Two classes of initiators (e.g. Figure 1) with different decomposition kinetics are used. TBPEH is a peroxide with its half life time in the range of seconds at reaction conditions. Representing a more stable hydroperoxide, TOHP possesses a half life time of up to several hours. In order to enhance these characteristics even more, TBPEH is added to the reaction mixture at high temperatures while TOHP is adjoined at low temperatures with subsequent heating.

The structural properties of the received polymers and the state of the added agents are analyzed by (LS-) GPC, IR and high temperature NMR.

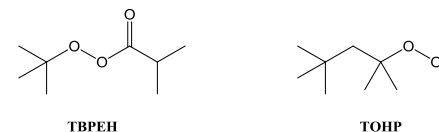


Figure 1: Mid-temperature initiator TBPEH (Tertbutyl-per-2-ethyl hexanoate) and high-temperature initiator TOHP (1,1,3,3-Tetramethylbutyl hydroperoxide) used in different sessions to test the agents influence on the radical polymerization

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