Characterization and Properties Prediction of Multi-Modal Ziegler-HDPE

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Introduction

Introduction: Why is high density polyethylene important?

- Broad range of properties, density, flow-ability and mechanical properties

- Processing
  - Film blowing
  - Pipe extrusion
  - Injection molding
  - Blow molding

- Products
  - Caps & closures
  - Pipes, coating
  - Drums, containers, tanks
  - Healthcare
  - Films and tapes

> **Global demand (2018) HDPE to 99.6 MT**
> **Rise 4.5% per year**
> **Valued at $60-70 billion, expected to reach $85 billion in 2022**

Pipeline & Gas Journal, December 2014, Vol. 241, No. 12

Introduction: Typical HDPE Products

IBC

L-Ring drums

Bottles
Jerry-cans

Pipe for
PE80 or PE100 applications

Packaging
Hygenic

Introduction: PE product design and requirements

➢ HDPE Product Performance

Processability

– Easy flowing or High melt-strength
– Good surface quality
– Processability at high throughput
– Controlled crystallization

- Control melt viscosity
- Introduce Long-Chain-Branching
- Modify Mol. Weight Distribution

Mechanical Properties

– ESCR
– Impact resistance
– Stiffness
– other final product properties, e.g. optics, organoleptics…

- Decrease melt viscosity
- Introduce comonomer (C4, C6)
- Control molecular structure

→ Find the optimal balance

Introduction: Challenges in HPDE Characterization

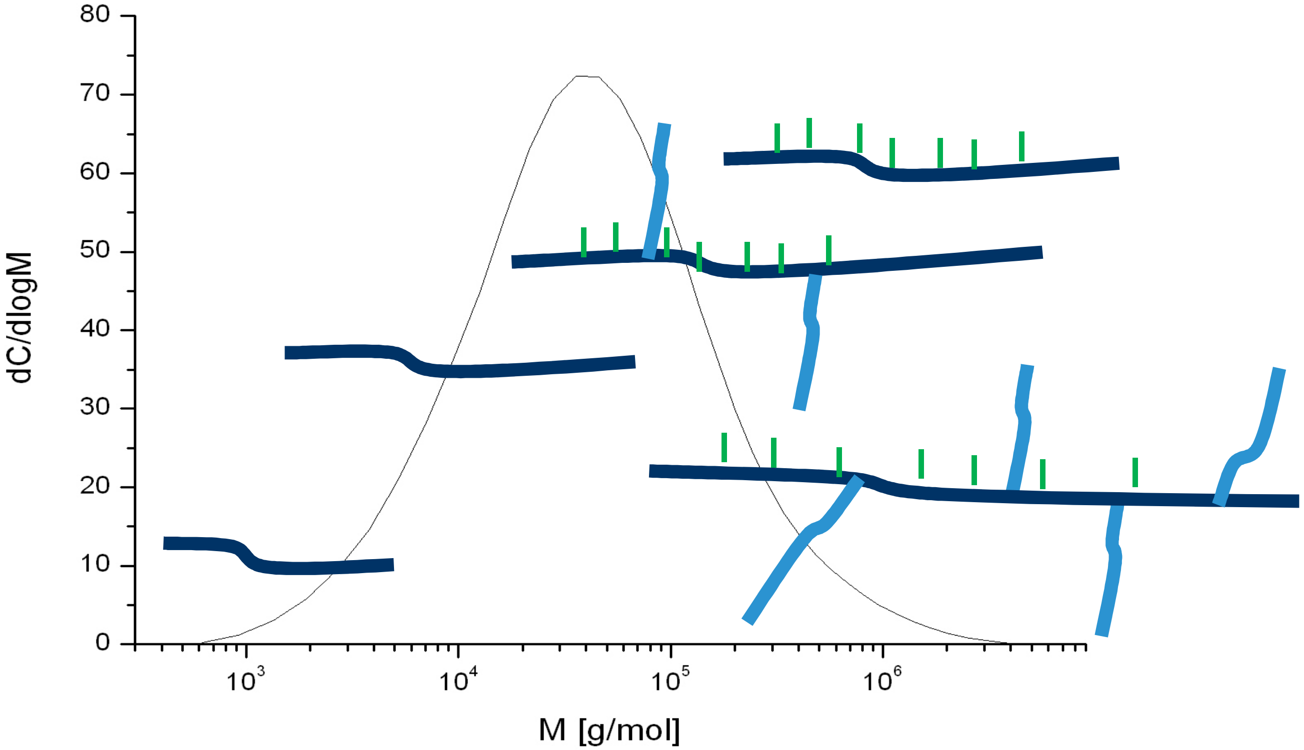
- Molecular structure:
  - Broad molecular weight distribution
  - Long-chain branching degree, type and distribution
  - Short-chain branching (comonomer) degree and distribution

- Technology/Catalyst
  - Cr-based, Ziegler-based
  - Gas-phase, fluidized bed single reactor or cascade
  - Slurry; CSTR in cascade, Loops, single reactor or cascade

- Physical/Chemical properties
  - Semi-crystalline polymer, thermorheologically complex
  - Strong dependence of rheology on mol. weight
  - Molecular weights from 10^3 to 10^7 g/mol, polydispersities from 3 to ~30-60
  - Solubility only at high temperatures and specific solvents

Introduction: Molecular structure of High Density Polyethylene

- Complex structure
  - Distribution of different mol. weights and structures (LCB)
  - Distribution of comonomer SCB (butene, hexene, octene…)

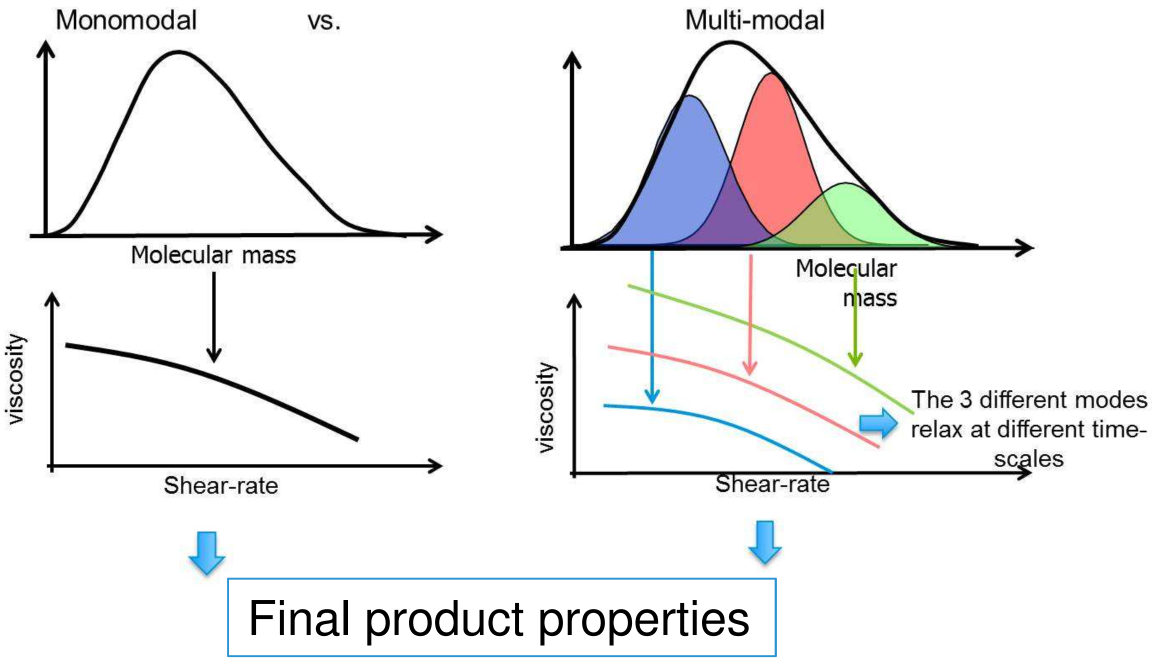


Introduction on Multi-modal PE

- HDPE based on Cr-catalyst → unimodal HDPE - very broad MWD
- Multi-modal Ziegler-type HDPE increasingly important and applicable

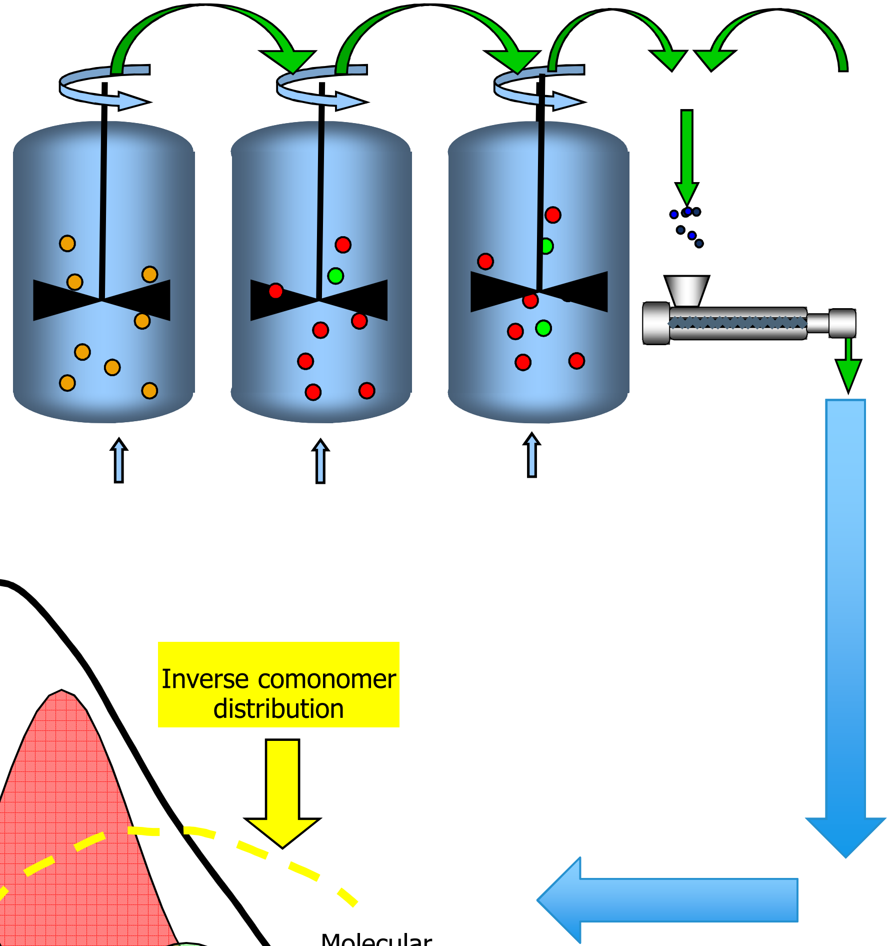
→new class of materials: Cascade process, such as the *Hostalen* ACP or *Hyperzone* Processes

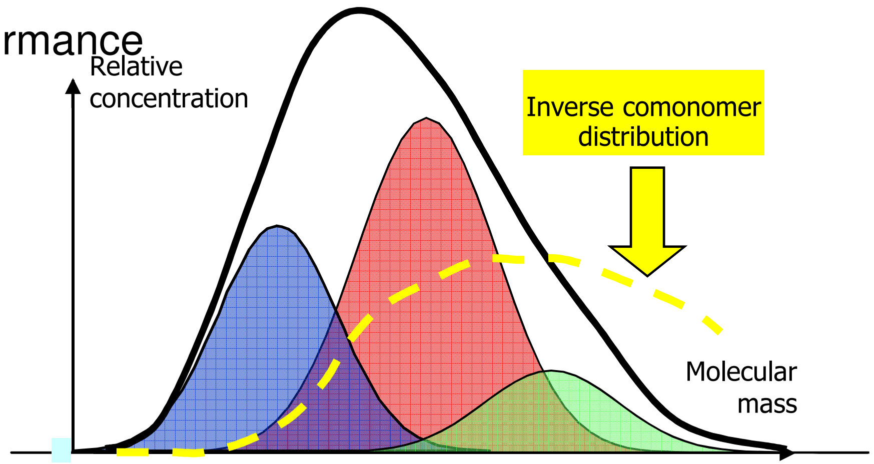
- Significant advantages, i.e. in terms of mechanical properties/processability balance



Example of multi-modal HDPE Technology: *Hostalen* ACP

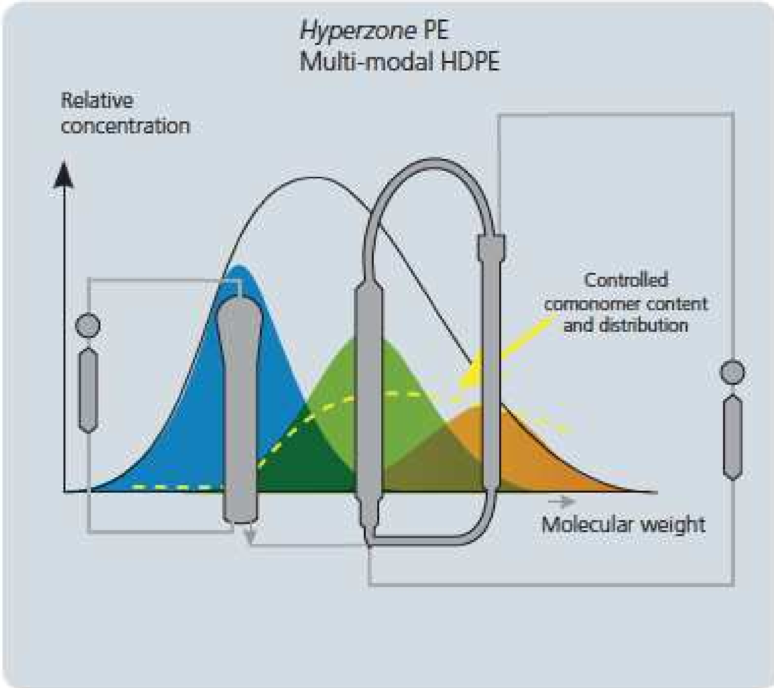
- *Hostalen* ACP Process: Established method of choice for producing HDPE (>2 M tonnes/a capacity)
- Tailored properties by an optimized reaction process and catalyst system
- Good balance between properties and processability → multi-modal process
  - Adjusting MW and branching separately
  - Consistent reactor engineering
  - Catalyst quality and performance





Example of multi-modal HDPE Technology: *Hyperzone* PE

- The unique process characteristics generate a precisely tailored molecular design to meet customers' demanding processing and product requirements
- The versatile technology will be able to supply all "Ziegler" and "Chromium" HDPE markets and applications using only Ziegler chemistry and with a competitive cost position
- Catalyst is injected into the first fluidized bed reactor, raw materials are fed to the separate reaction zones
- The characteristics of the multi-zone circulating reactor ensure intimate molecular scale mixing of the higher and lower molecular weight polymer fractions produced in the different zones, resulting in highly homogeneous products with exceptional surface and mechanical properties.



Characterization Methodology

Characterization and Process-ability Prediction

- Standard/traditional characterization methods developed for unimodal (linear) PE
  - Std. characterization on final granulate
  - MFI, density

→ **Low Resolution on changes within each mode/fraction/component**

- Challenges in:
  - Correlation of molecular parameters or linear rheology (e.g. M_w, η_0) to final product processing-performance
  - Discriminating “good” and “bad” performers
  - Prediction of final product properties
    - Processability
    - Surface/optics
    - Mechanical properties (stiffness, ESCR, impact)

Characterization and Process-ability Prediction

➢ **Advanced – Detailed Characterization required**

1. Molecular Characterization with GPC-MALLS / GPC / fractionation
   - Final product and intermediate reactor samples

2. Std. Linear Rheology (Flow curves)
   - Final product and intermediate reactor samples

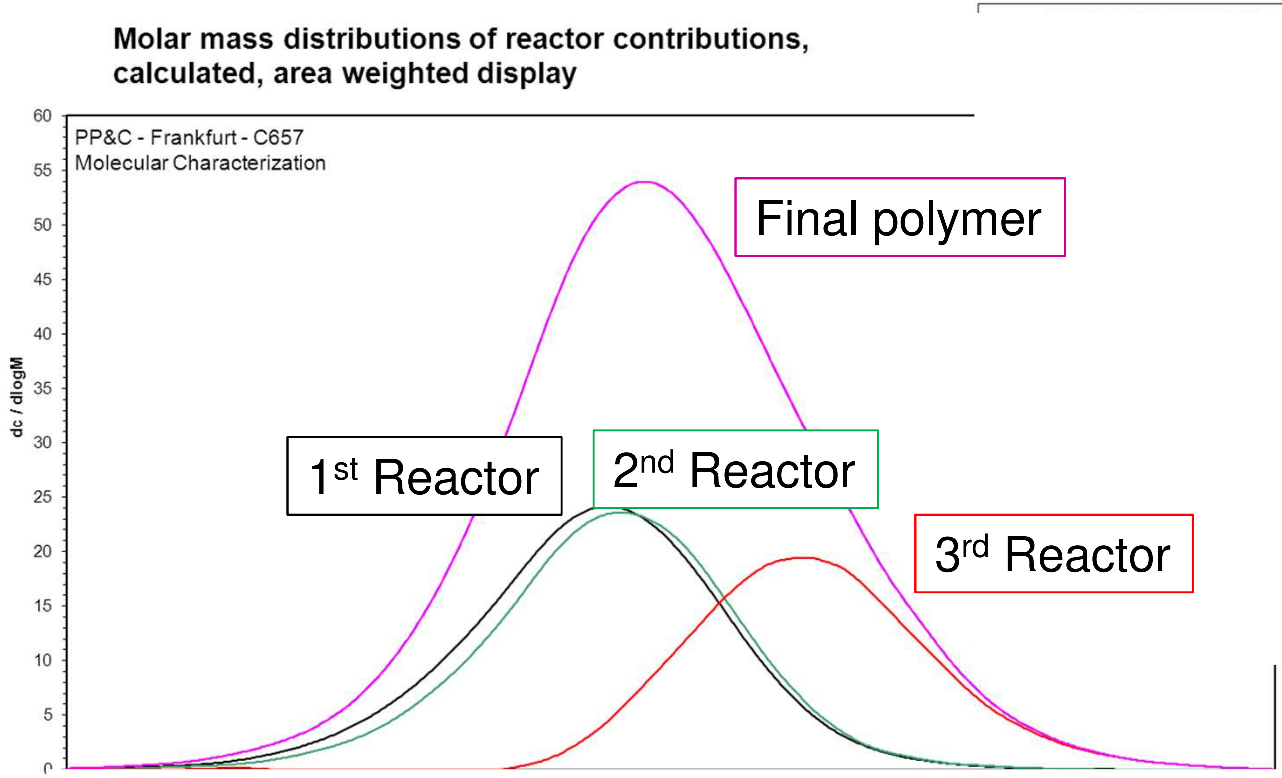
2. Non-linear Rheology and Process-ability prediction
   - Elongational viscosity or Sharkskin test and Capillary rheometry

3. Prediction of final product properties
   - Impact strength and fast stress-crack resistance (FNCT)
   - Dimension stability and optics

4. Process simulation and polymer structure prediction
   - Model low-pressure catalytic polymerization

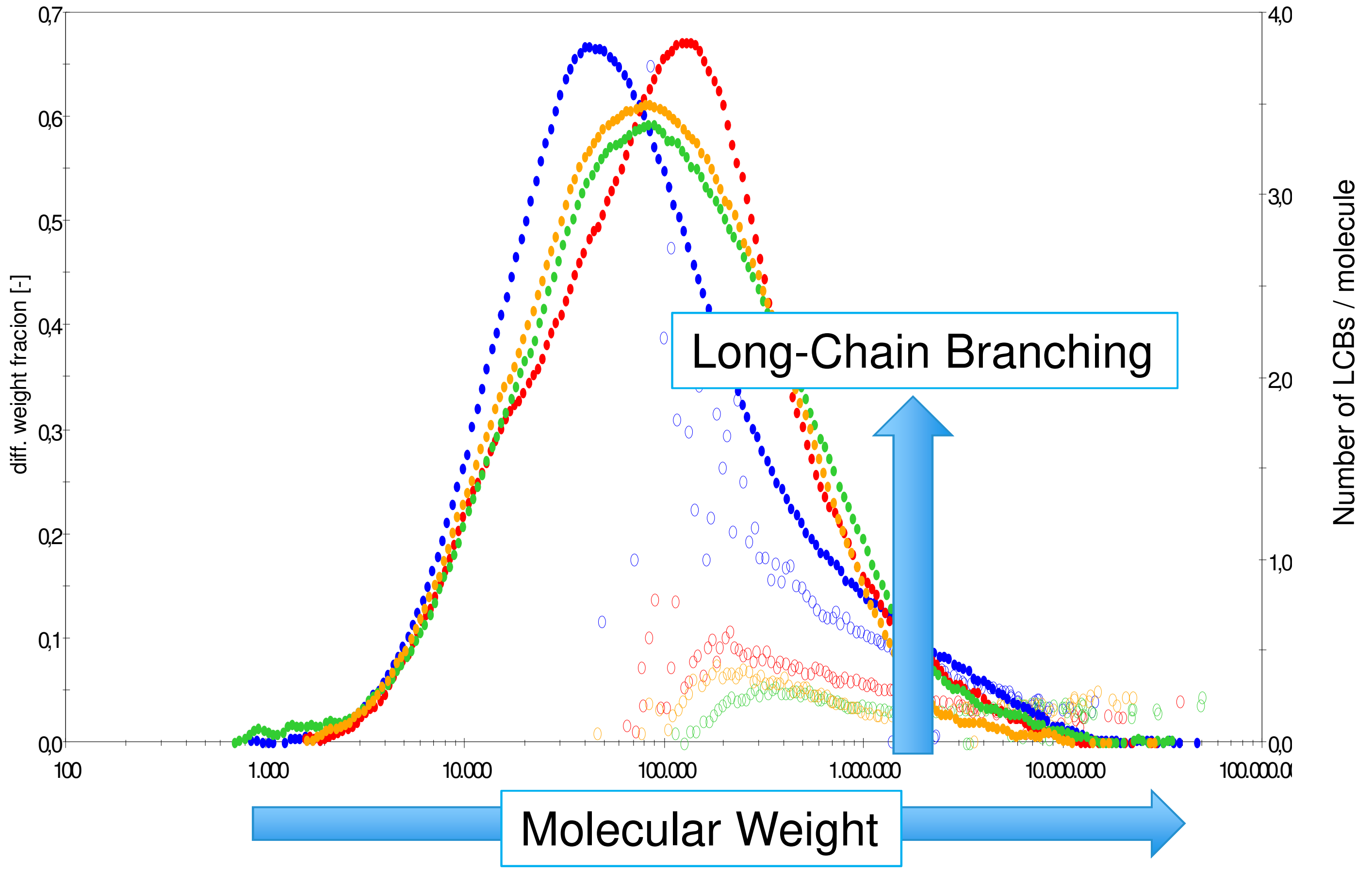
Molecular Characterization: Mol. Weight Distribution

- Gel Permeation Chromatography
  - Deep insight in molecular weight distribution
  - Measure reactor samples and determine individual reactor contribution



Molecular Characterization: MWD and LCB

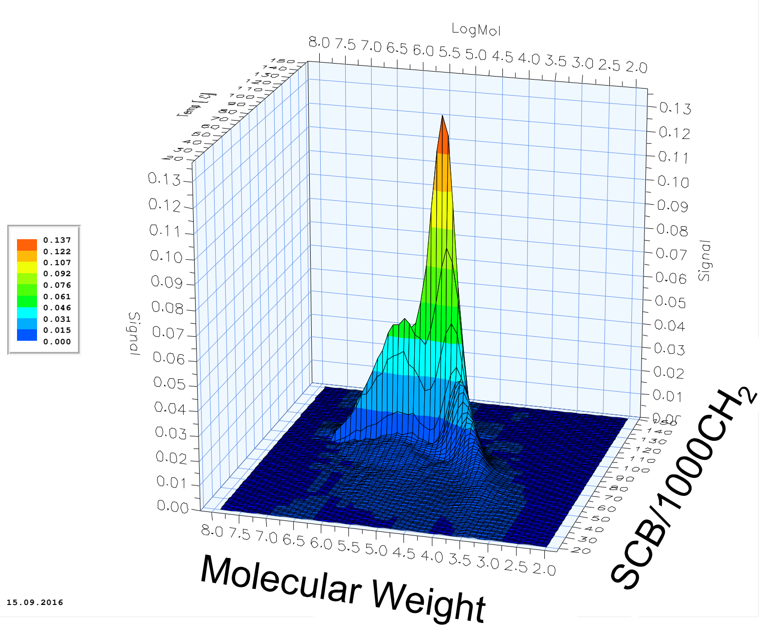
- GPC coupled with Multi-Angle-Laser Light Scattering
  - Measure molecule size → determine the branching degree



Molecular Characterization: Quantify MWD and SCB

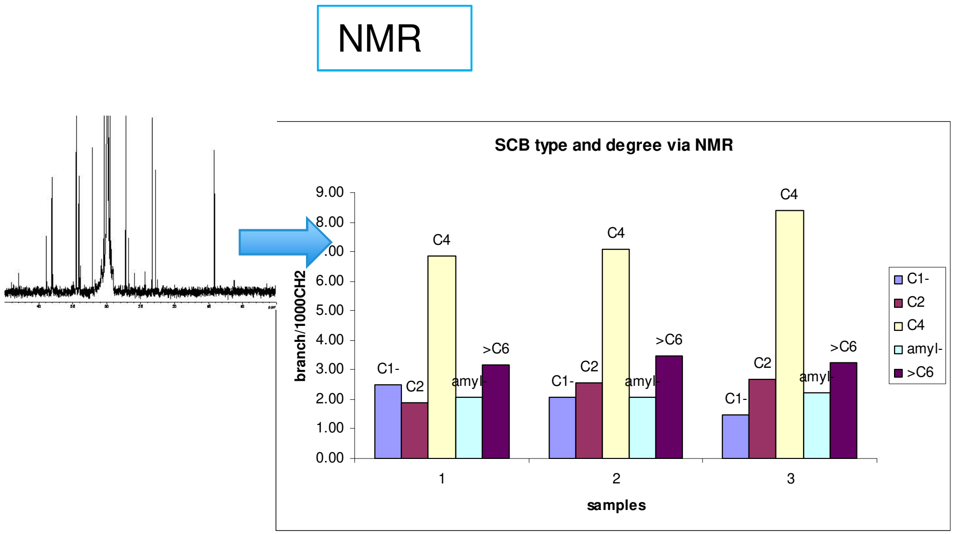
- SCB average degree correlates to density
  - Distribution of SCB on MWD extremely important
- Comonomer distribution determined by fractionation techniques
  - GPC-IR5 for MWD and comonomer distribution
  - aTREF-GPC for accurately determine composition and fingerprinting

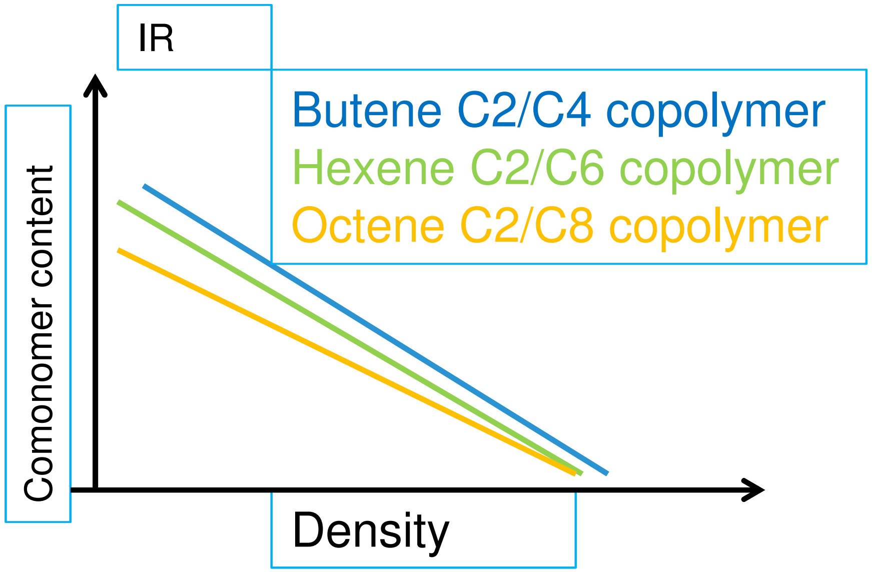
Fractionation according to SCB and MWD



Molecular Characterization: Quantify MWD and SCB

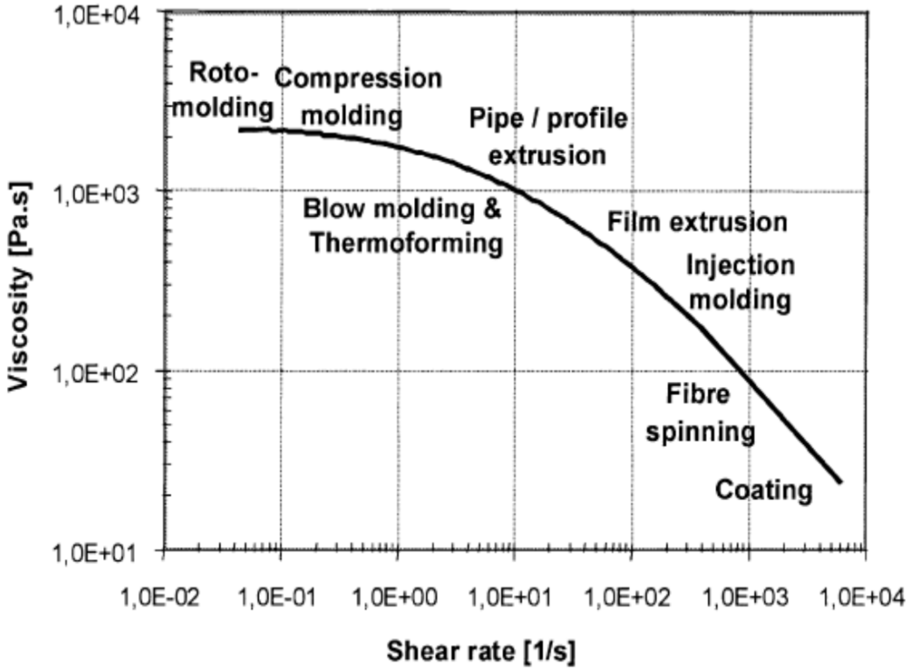
- Comonomer incorporation quantified by:
  - NMR detects the type and concentration of SCB
  - IR for determining the type and average concentration of side-chains





Rheology: Flow properties

- Flow properties correlated to structure and processabililty



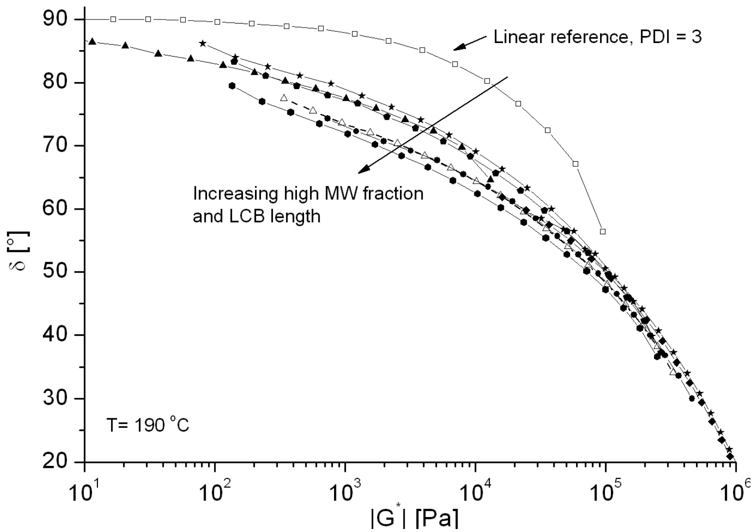
- Material structure
- Established methods
- Difficult extrapolation to processing conditions

- Process relevant properties
- Challenging measurement and interpretation

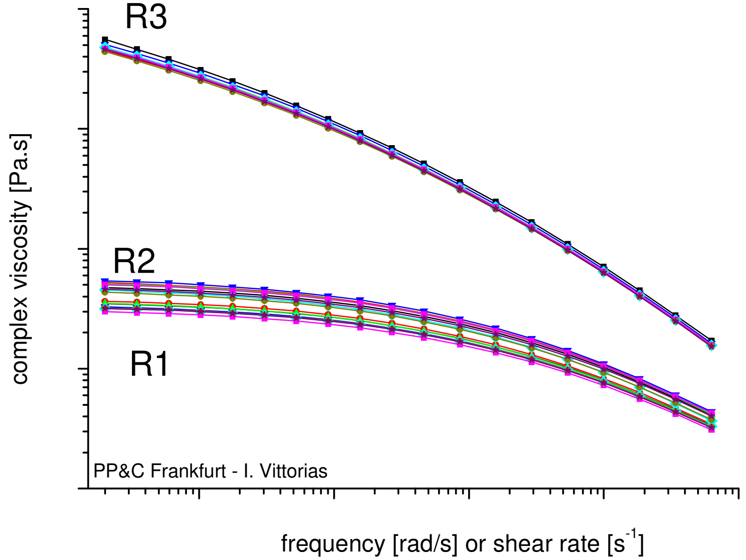
Rheology – The LCB issue

- Linear PE
  - ✓ High density, high crystallinity - Desirable mechanical properties
  - \- Inferior processability
- Introduction of long- (M_{branch}>M_e) chain branching, LCB
  - ✓ Enhanced Processability - Reduction of extrusion cost
  - \- Inferior mechanical properties, impact-strength, ESCR

Van Gurp-Palmen Plots to detect rheologically effective LCB

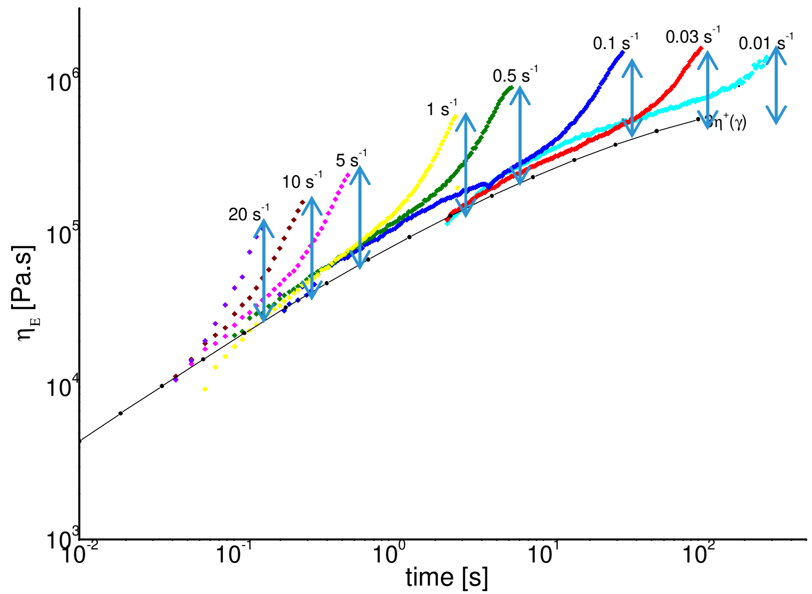


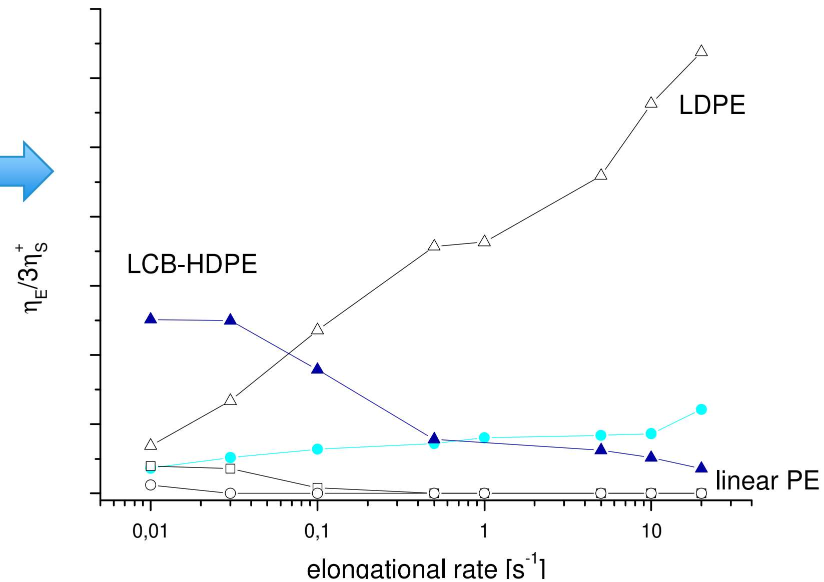
Rheology on reactor samples
Calculation of individual contribution



Rheology – Determine LCB with elongational rheology

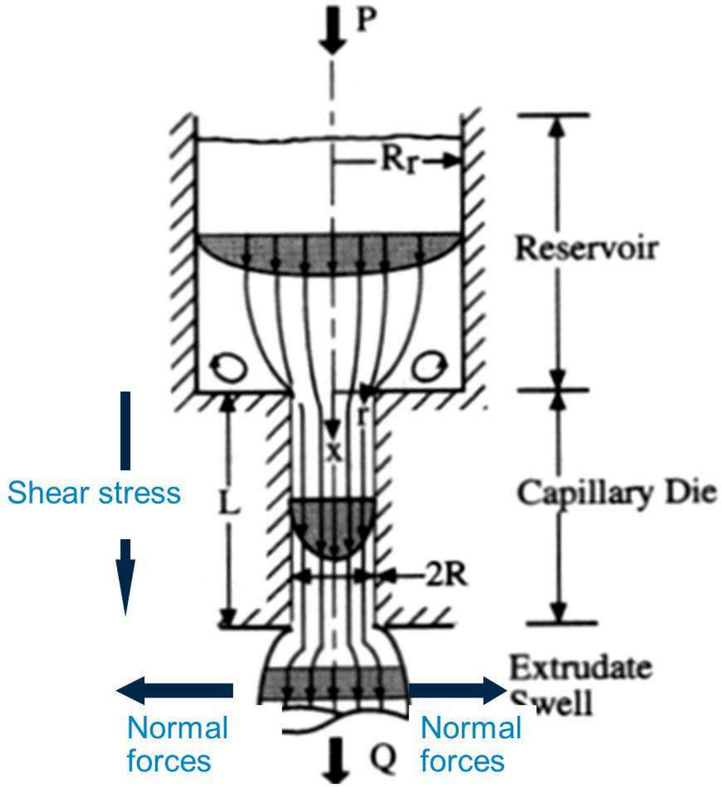
- Elongational viscosity: Strain hardening at different elongational rates
  - Processing relevant deformations – non-linear test
  - Distinguish LCB from MWD effects
  - Challenging measurement





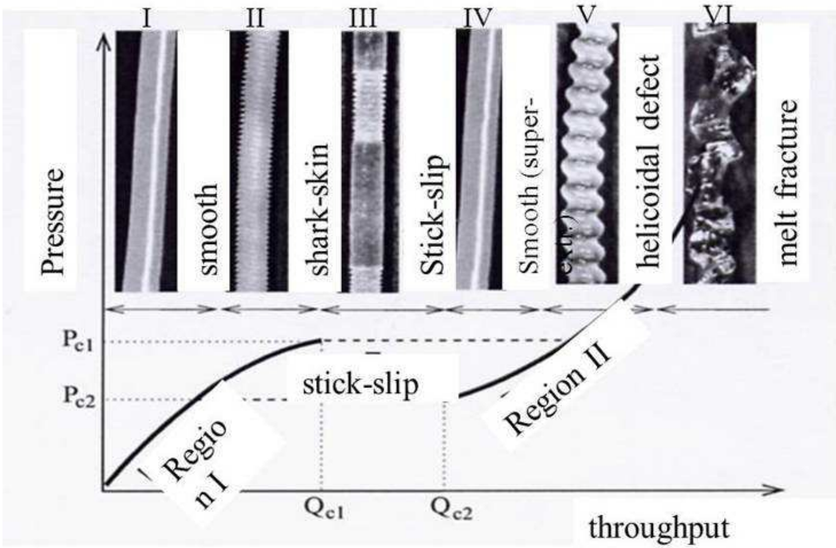
Prediction of process-ability with capillary rheometry

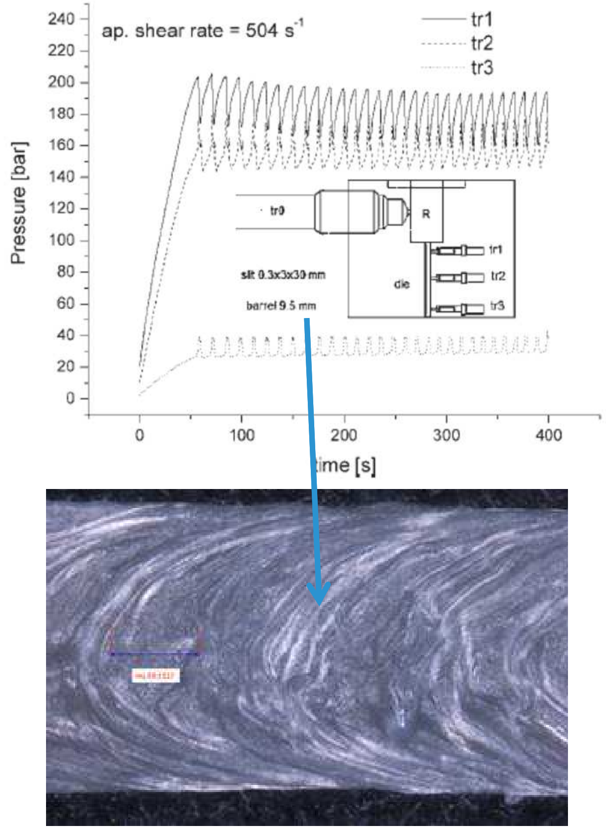
- Simulating processing conditions in the lab and connecting structure to processing
- Combined with different techniques to predict performance under processing conditions
  - Extrudate-swell and wall-thickness
  - Surface quality
  - Dimension stability



Rheology and Processing

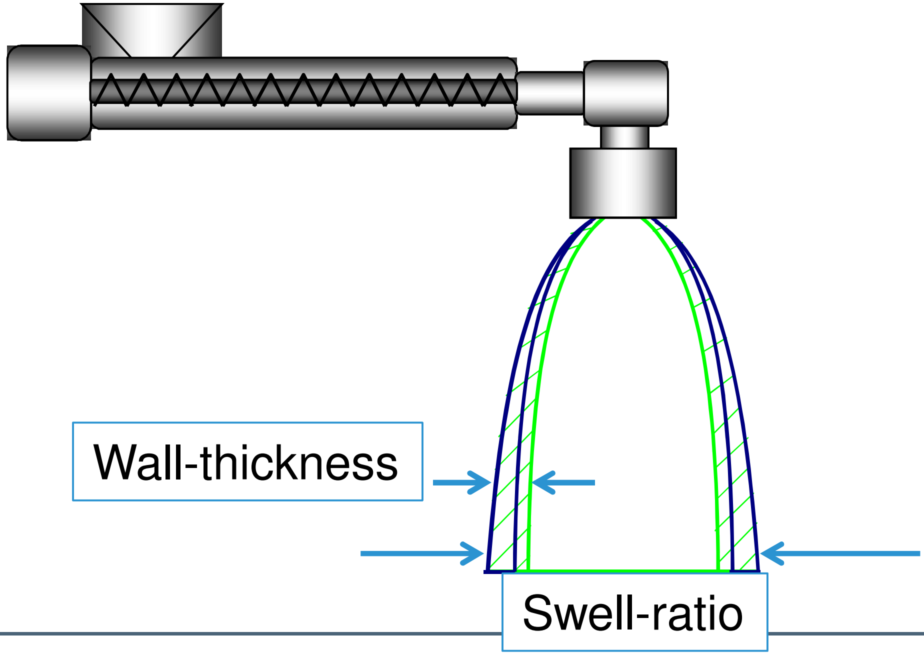
- Large deformation rates (proportional to extrusion throughput) → extrudate distortions – Product failure/Low quality
- Measure and quantify surface defects (Sharkskin measurement)

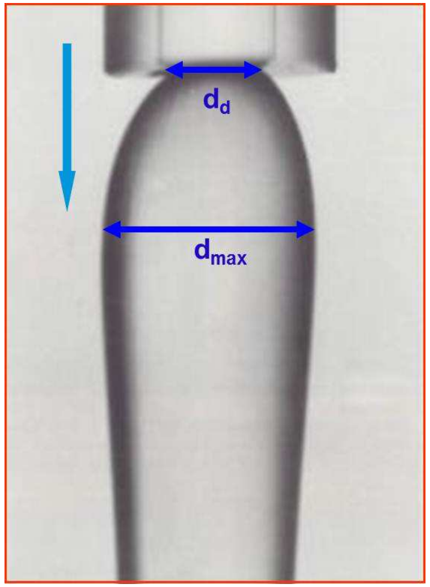




Process-ability and wall-thickness prediction

- Wall-thickness and parison-swell is a different process
  - Two different properties
  - Important for process-ability and final product dimensions
- Test in a capillary rheometer equipped with a ring-die of same geometry as in Blow-Moulding process
  - Low shear-rates but controlled and reproducible test

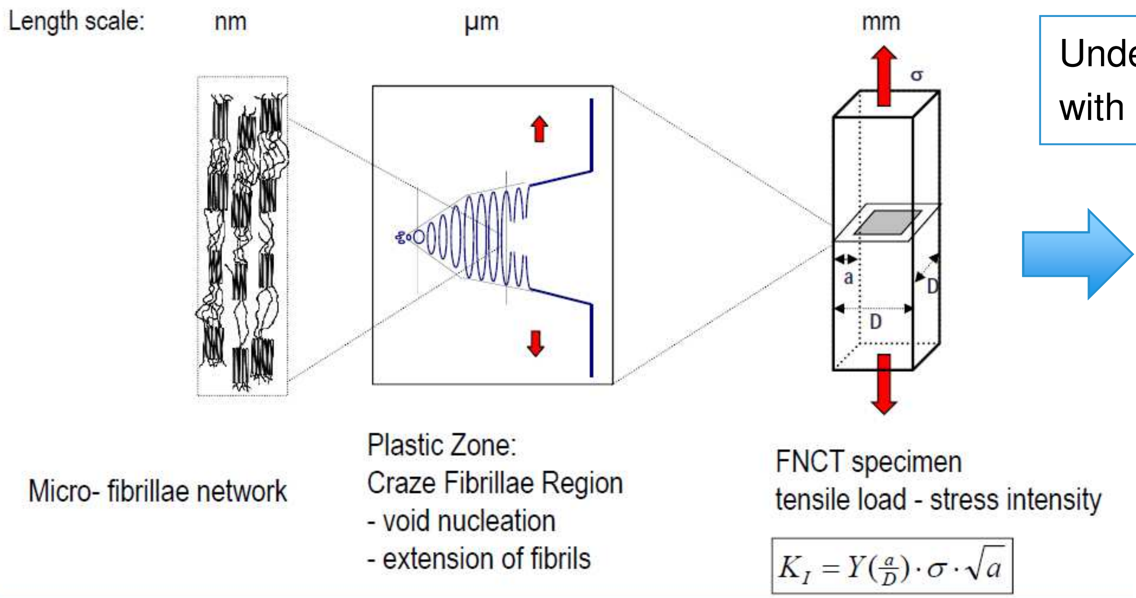




Mechanical Properites

- Impact strength
- ESCR quantified by Full Notch Creep Test
- Accelerate crack propagation → shorten measurement times

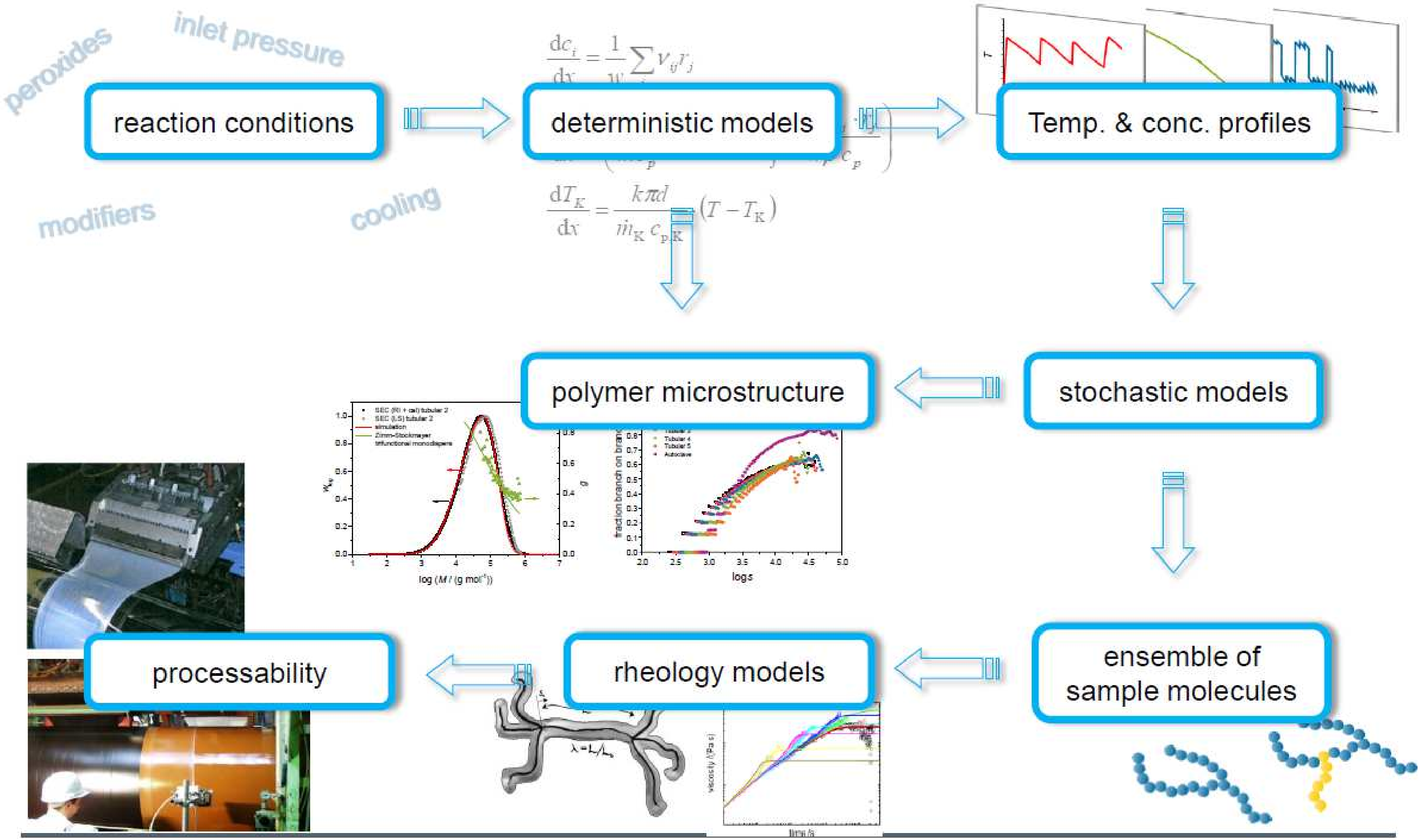
→ Support development of new materials



Under stress at high temperature in bath with water/surfactant solution

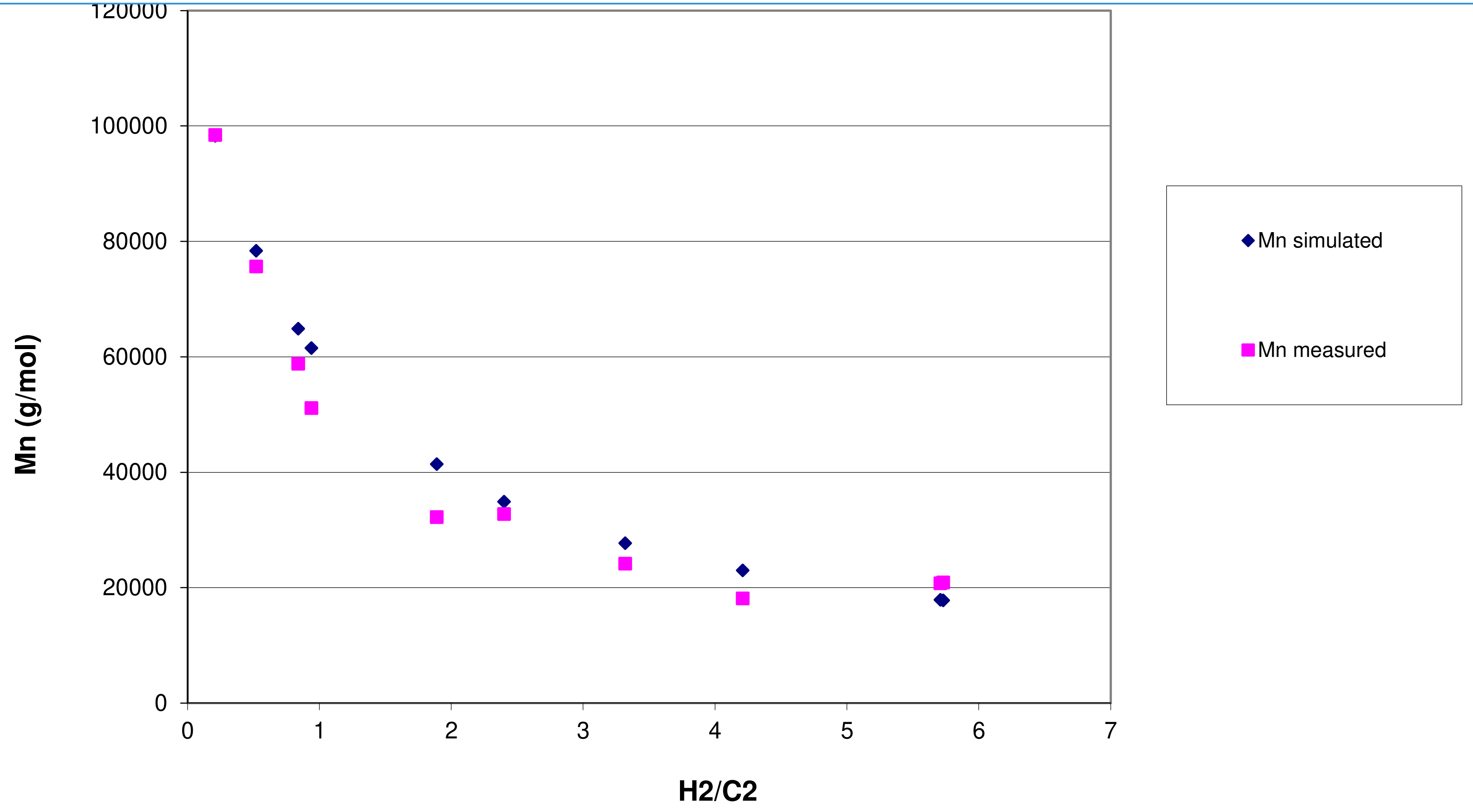
- optimized non-corrosive equipment (Fa. OCS Witten, Germany)
- quality control of the bath is facilitated

Modelling: closing the loop



Modelling: HDPE Correlation Reaction conditions to Structure

Control of molar mass (Mn): Prediction vs. experimental as a function of H2/C2

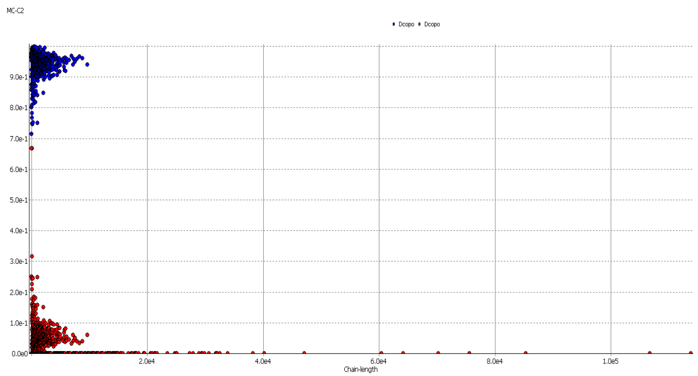


Modelling: HDPE Correlation Reaction conditions to Structure

- Predict comonomer distribution (SCB)
- Compare prediction to experimental

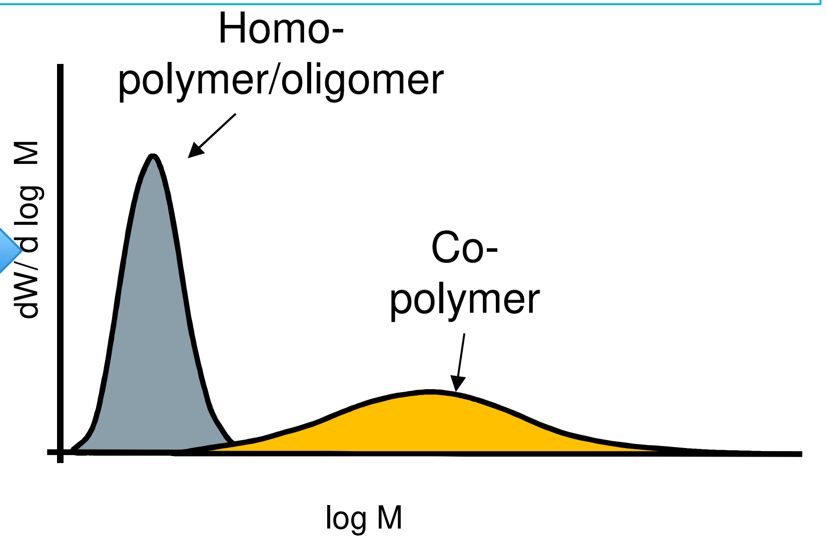
MC Prediction of SCB as a function of MW

C2 / C4 Concentration



Chain length

Experimental Comonomer distribution (CFC)

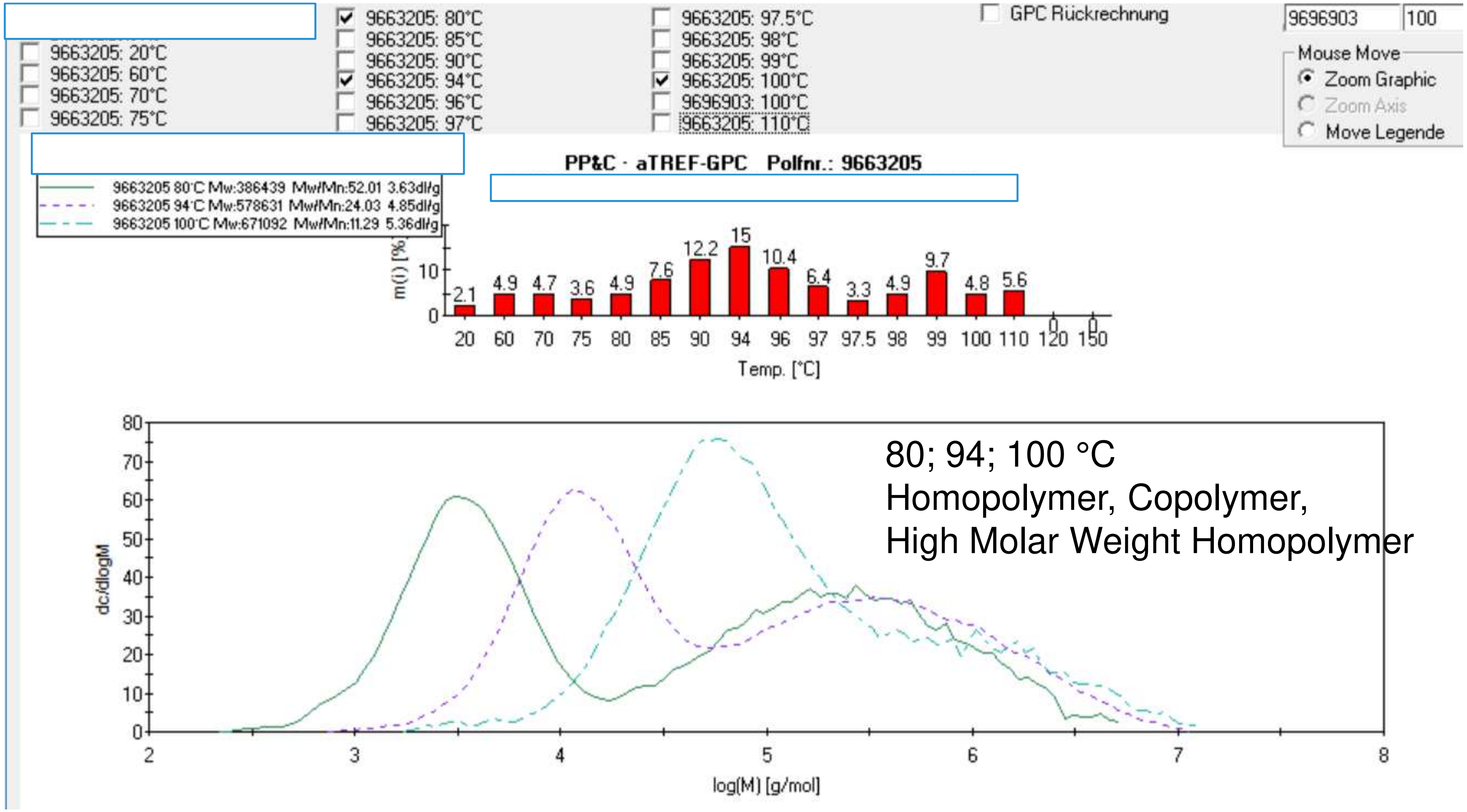


- Correlation copolymer fraction to FNCT, Creep, Impact

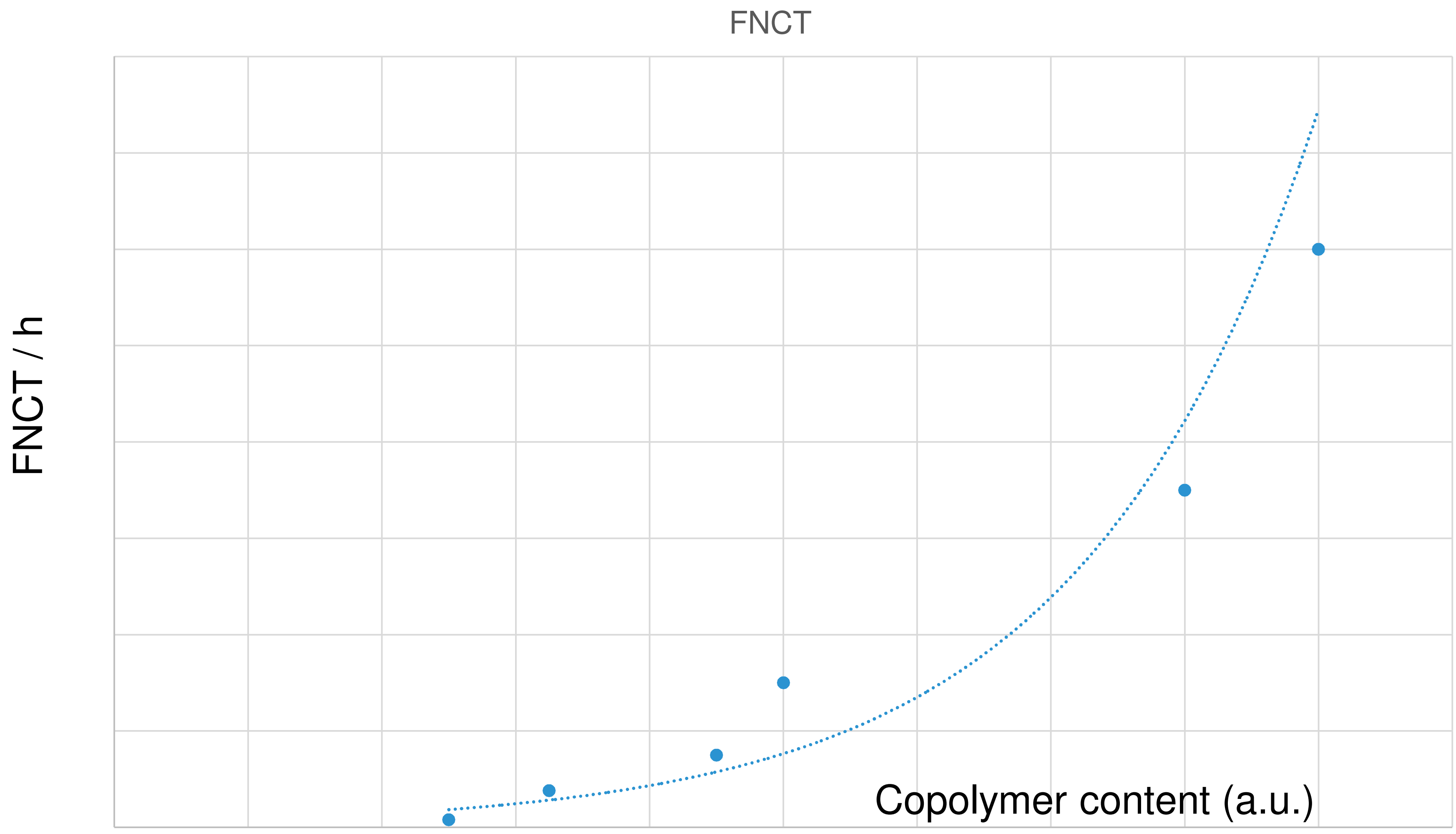
Cross Fractionation Chromatography (CFC)

- A number of fractions are eluted automatically
- Elution temperature ranges from 20 till 120 °C
- Copolymers of different C4 or C6 incorporation are determined
- Temperature ⇔ C4 incorporation ⇔ CH3/1000C
- In addition low molar weight homopolymer and standard homopolymer is evaluated
- Low molar weight homopolymer and high molar weight copolymer are eluting by chance at the the same temperature => separation by mathematical fit of the GPC curves
- At higher temperatures higher molar weight PE is eluting
- ESCR properties (Pipe) properties are analyzed by FNCT
- FNCT is correlated to copolymer content and copolymer molar mass

Cross Fractionation Chromatography



FNCT controlled by Copolymer Content



FNCT controlled my Molar Weight Mw (Copolymer)

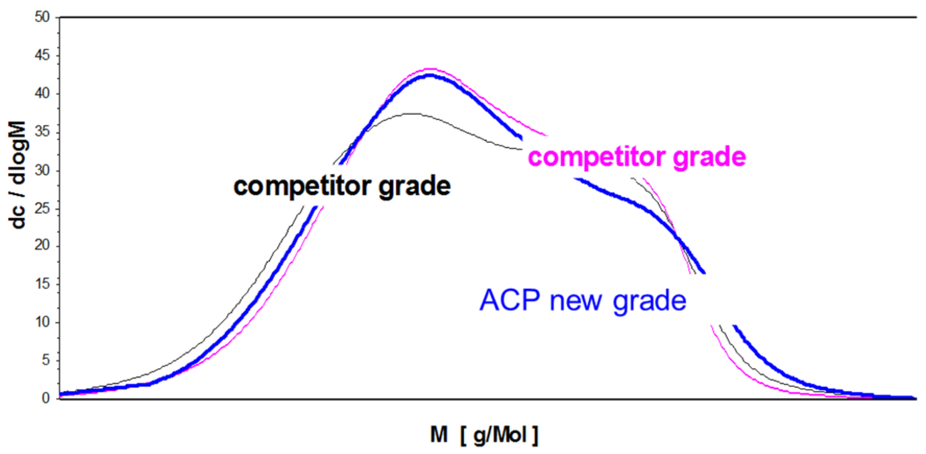
Run	Sample	Copo amount 60 - 90 °C TREF [%]	Copo Mw TREF [a.u.]	Density [g/cm^3]	FNCT (90°C; 5 MPa ESA 1.2)
one	R3	15%	100	0.9489	**70 h**
Two	R3	16%	156	0.9485	**167 h**
three	R3	17%	120	0.9481	**100 h**

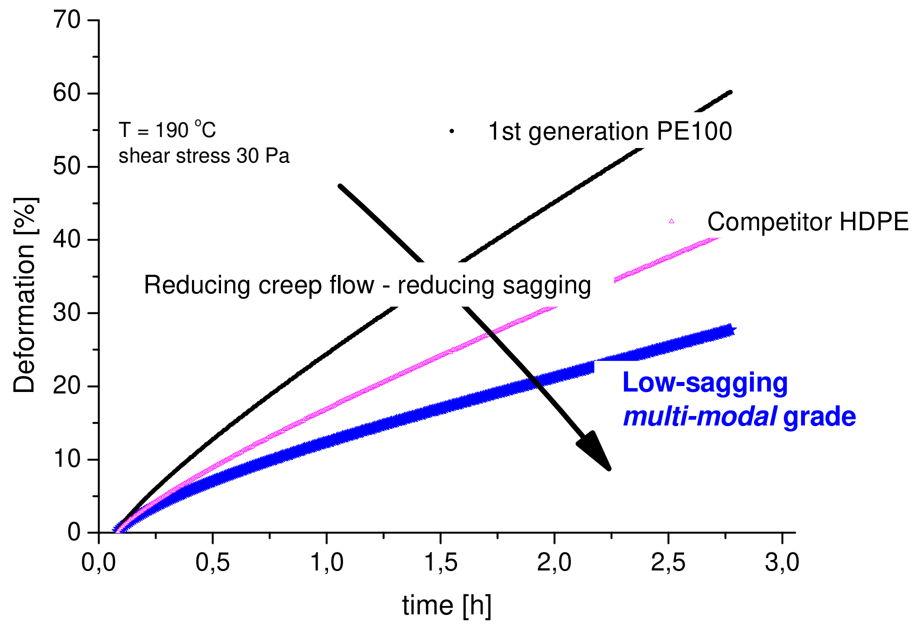
Case Studies

HDPE for pressure-pipe-applications:

- Required excellent Enviromental Stress Crack Resistance (ESCR)
  - Low creep in solid-state under pressure
  - Sufficient flowability for pipes of different sizes (fast and slow-extrusion) with low sagging

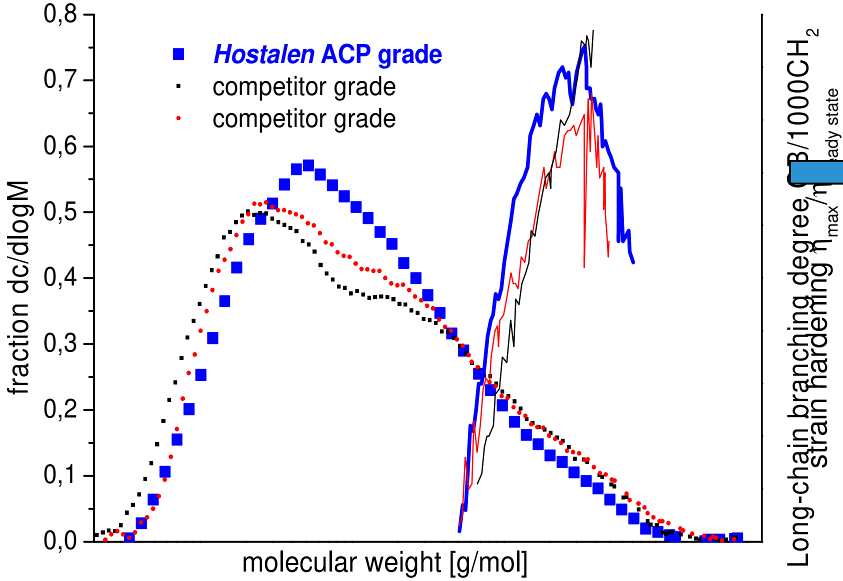
➢ Control SCB and MWD → ✓Increase flowability and ESCR

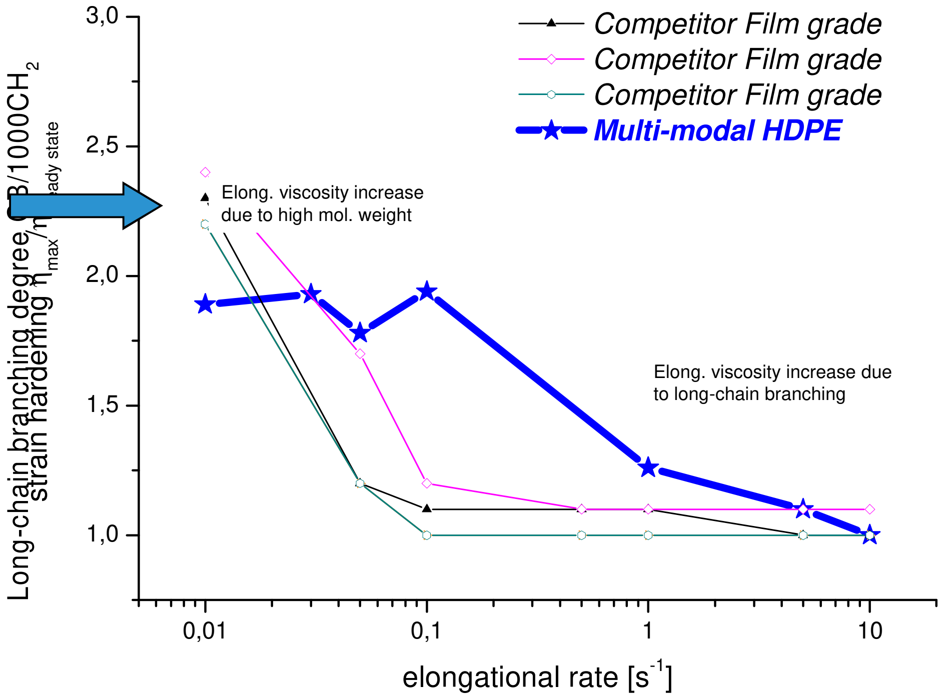




Films with Excellent Processability and Improved Impact Strength

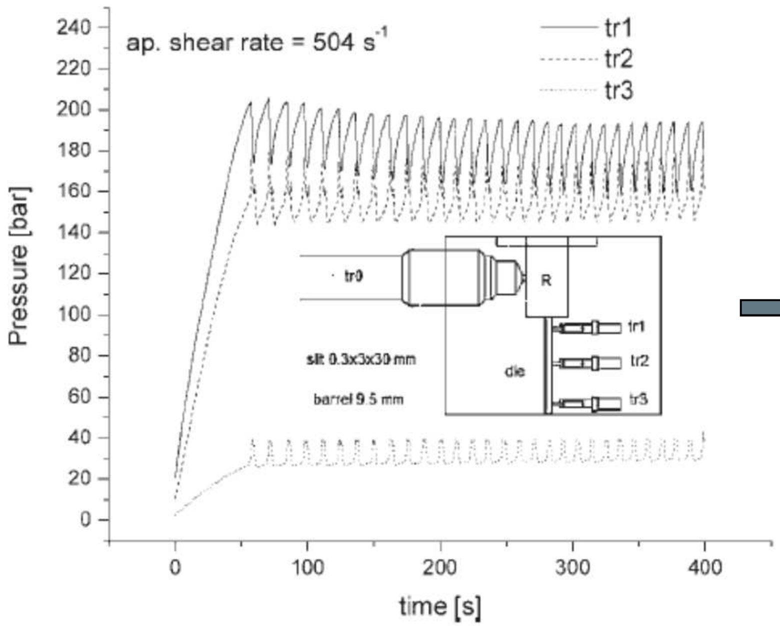
➢Increase LCB ✓Increase Strain Hardening

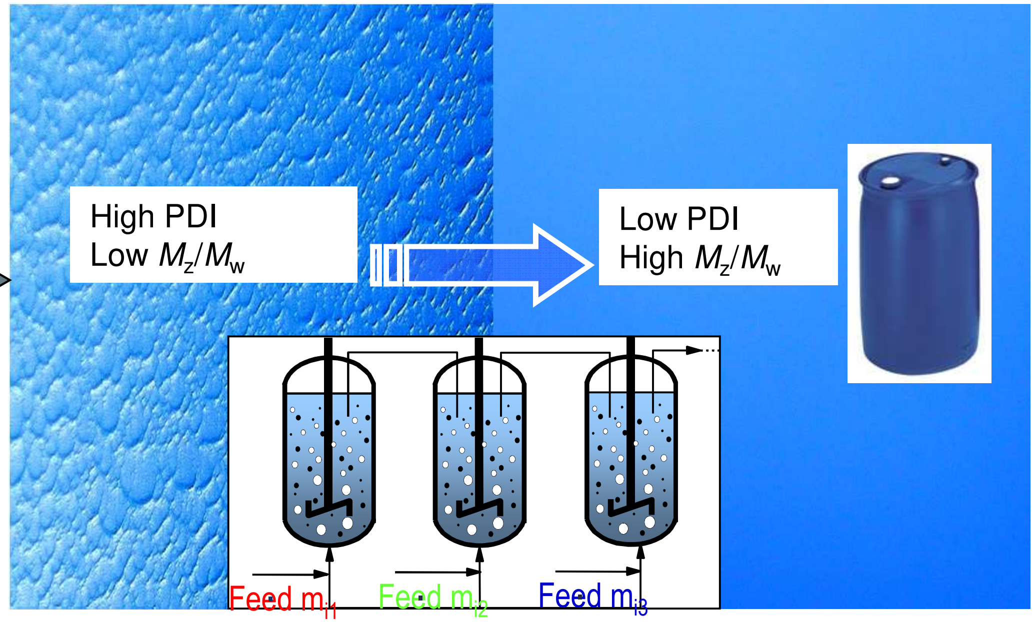




Flow-instabilities and surface quality

- ➢ Large deformation rates (proportional to extrusion throughput)
  - → Surface distortions – Product failure
- ➢ Predict the critical shear-rates and quantify the severity of flow-instabilities
  - Under process-relevant conditions: Lab-test → Sharkskin test
- ➢ Connect to molecular structure → fine-tune
  - Cascade process offers more degrees of freedom to suppress flow instabilities





Summary

Summary

- HDPE is important for numerous applications and exhibits a broad range of properties
- Control the MWD, LCB and comonomer incorporation

➢ **New Process for Multi-modal Ziegler HDPE: *Hyperzone* Technology**

- Supreme process flexibility and State-of-the art Ziegler catalyst/co-catalyst systems
- Shift to a new class of polymers in the Mechanical strength vs. Process-ability relation

➢ **Methodology to connect Chemistry to final product properties**

- ➢ MWD, LCB, SCB distribution with GPC-MALLS, CFC, linear rheology → Determine structure
- ➢ Non-linear rheology (elongation, capillary) → Predict process-ability
- ➢ Model process → Predict polymer structure
  - ➢ Input reactor type/conditions and predict produced MWD, comonomer and LCB distribution
  - ➢ Predict flow- and mechanical properties

✓ **Create tailor-made PE products with optimum final properties**

✓ **Close the loop: Chemistry ↔ Final Product Properties**

Connect catalyst chemistry/reaction engineering to final product

- Kinetics
- Reactor

→

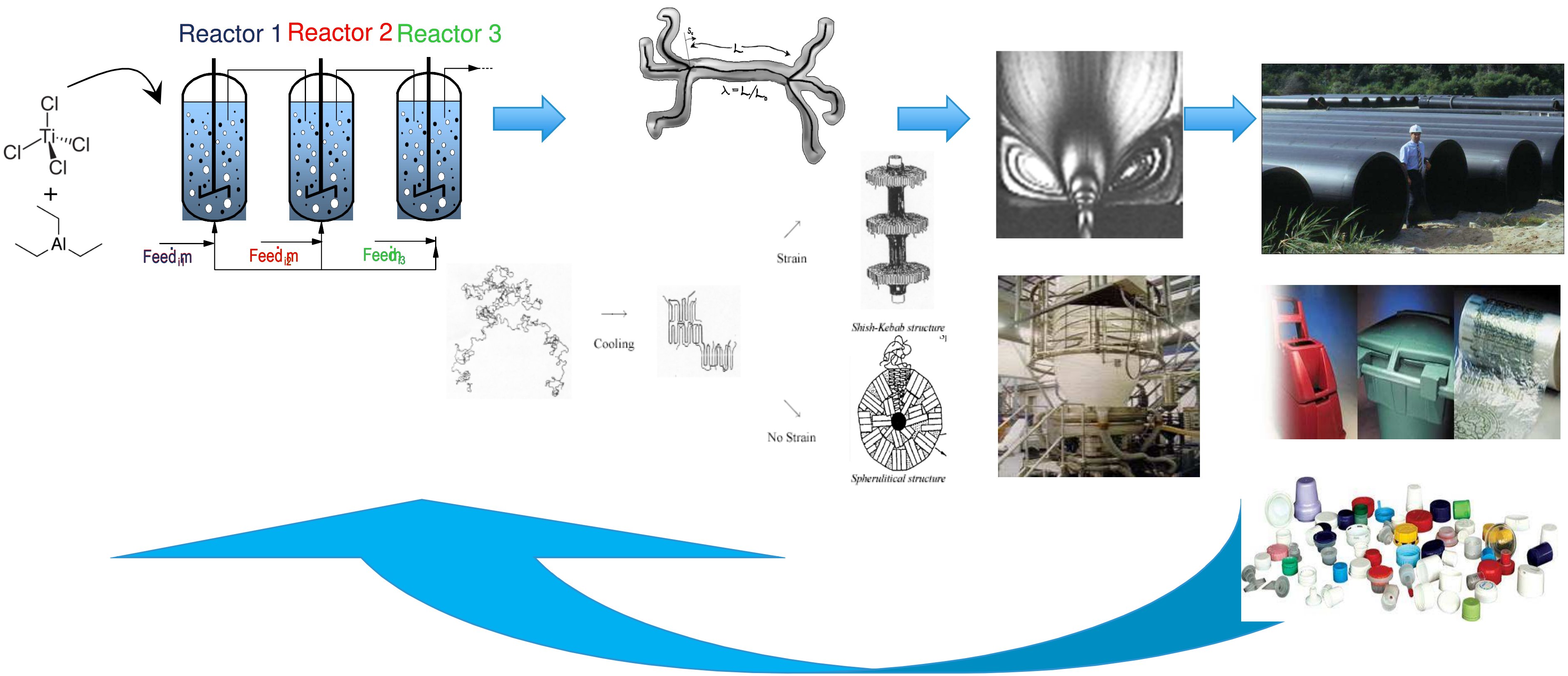
- Chain structure
- conformation

→

- Processing
- Flow/Crystallization

→

- Final product properties



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