# Bedeutung der GPC/SEC für Produktentwickluing, Qualitätssicherung und Umwelt

**Peter Kilz**

PSS, Mainz, Germany

PKilz@pss-polymer.com

# Why Bottom-Up Characterization?

- Knowledge-driven design of products
- Utilize structure-property-function relationships
- Apply fundamental knowledge
  for product development

Goal: faster / better products for specialized use

Key: property determination on molecular level

Technique: SEC with multiple detection

# Bottom-Up Product Development

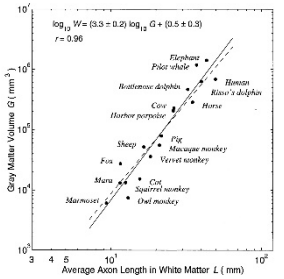
**Product**

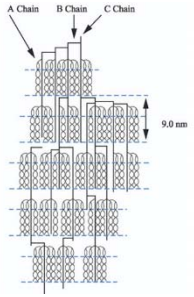
**Technical implementation**

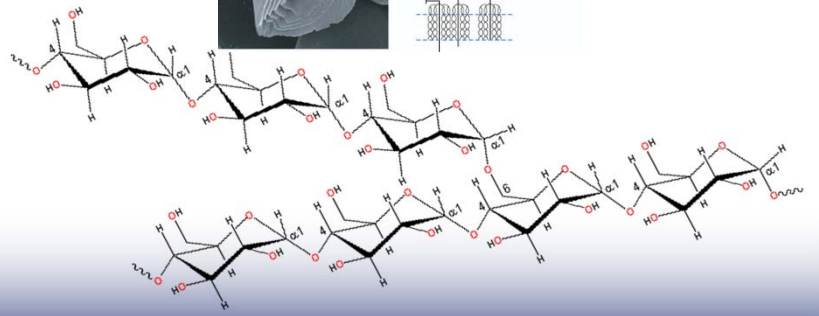
**Establish scaling rules**

**Understand interactions**

**Characterize molecular properties**



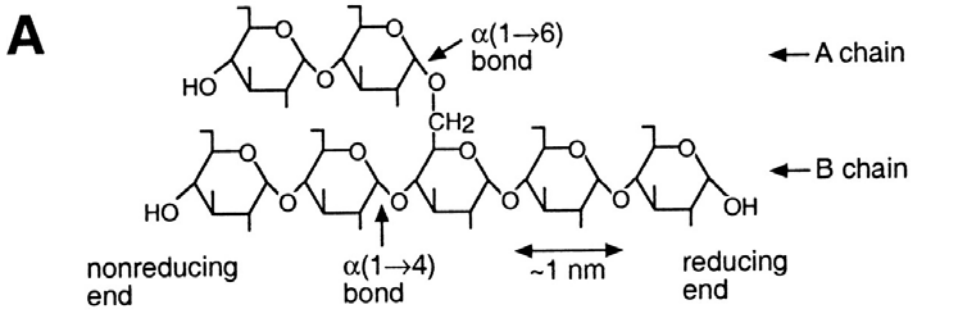
# Chromatography as Microscope

## Starch size domains

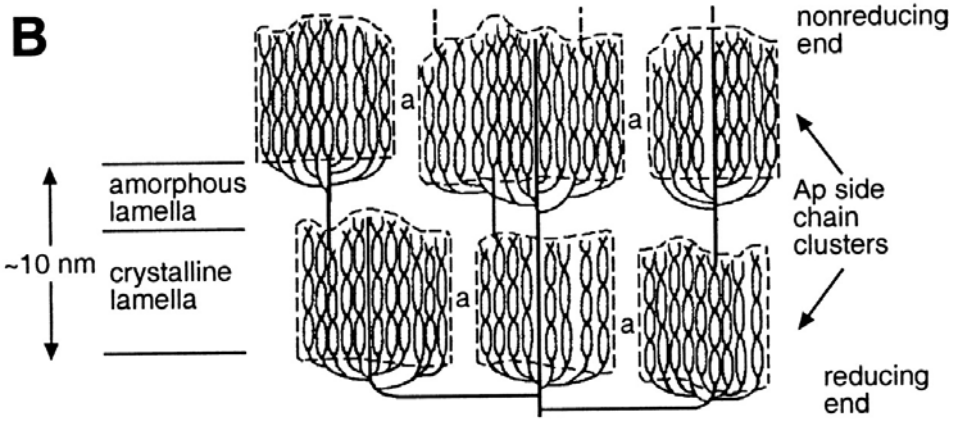
| | | | | |
|---|---|---|---|---|
|  | **Grain** | **cm** | **$10^{-3}$ m** | **macroscopic properties** |
|  | **Granules** | **µm** | **$10^{-6}$ m** | **application properties** |
|  | **Chains** | **nm** | **$10^{-9}$ m** | **molecular properties** |

# Elucidation of Starch Structure

## Starch structure levels



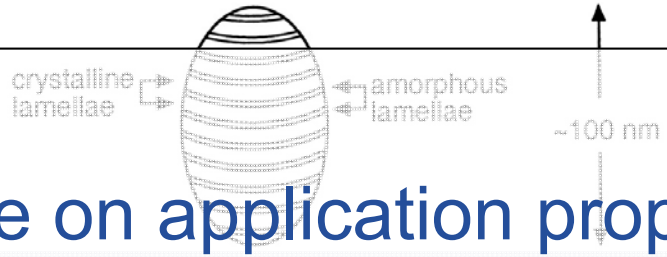

## Starch example of very complex macromolecule:




Co-existence of

- Molar mass distribution (MMD)
- Architecture distribution (MAD)
- End group distribution (FTD)
- Composition distribution (CCD)

…




**Todays focus:**
molar mass influence on application properties

# Dry- and Wet-milling Process and Products

## Similarities and Differences

Dry-Milling

- Deformation (Impact, shear)
- Crushing (Impact, pressure)
- Very good CWB, CWS, F-T-S
- Energy necessary 84 kWh/kg

Wet-milling

- Deformation (Shear, scission)
- Tear to pieces (Shear)
- Good CWB, CWS, F-T-S
- Energy necessary 0.6 kWh/kg

Challenges in milled cereal products

- ++++ Sensory
  ++ Rheo-stability
  - - - Energy balance

- +++ Sensory
  +/- Rheo-stability
  ++++ Energy balance

# Application Properties of Wet-milled Starches

- **Maize starch**
  Gel formation: good
  Gel stability: very good
  Freeze-thaw stab very good
  Mouth feel: spongy

- **Wheat starch**
  Gel formation: good
  Gel stability: very good
  Freeze-thaw stab very good
  Mouth feel: smooth

**Develop structure – function relationship for milling**

- dependence on starch source
- influence on MMD
- structural changes

# Experimental

GPC/SEC performed with:

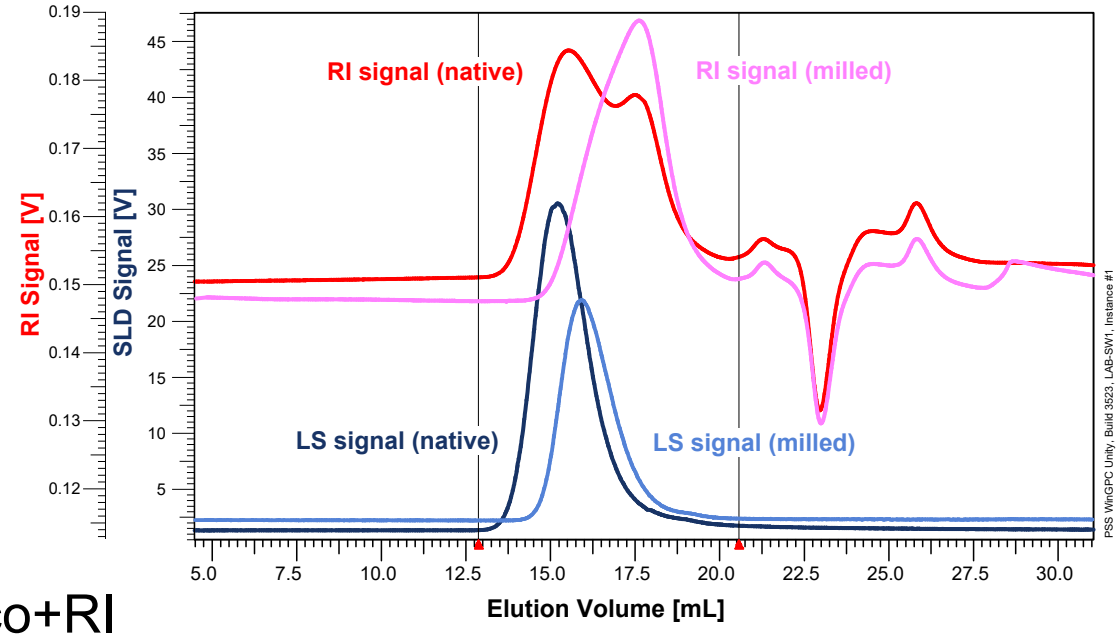
- PSS SECcurity GPC System
- PSS GPC columns
- PSS SLD7000 MALLS
- PSS DVD1260 Viscometer
- PSS calibration standards
- PSS WinGPC Software

# Maize Starch
# SEC-DV-MALLS

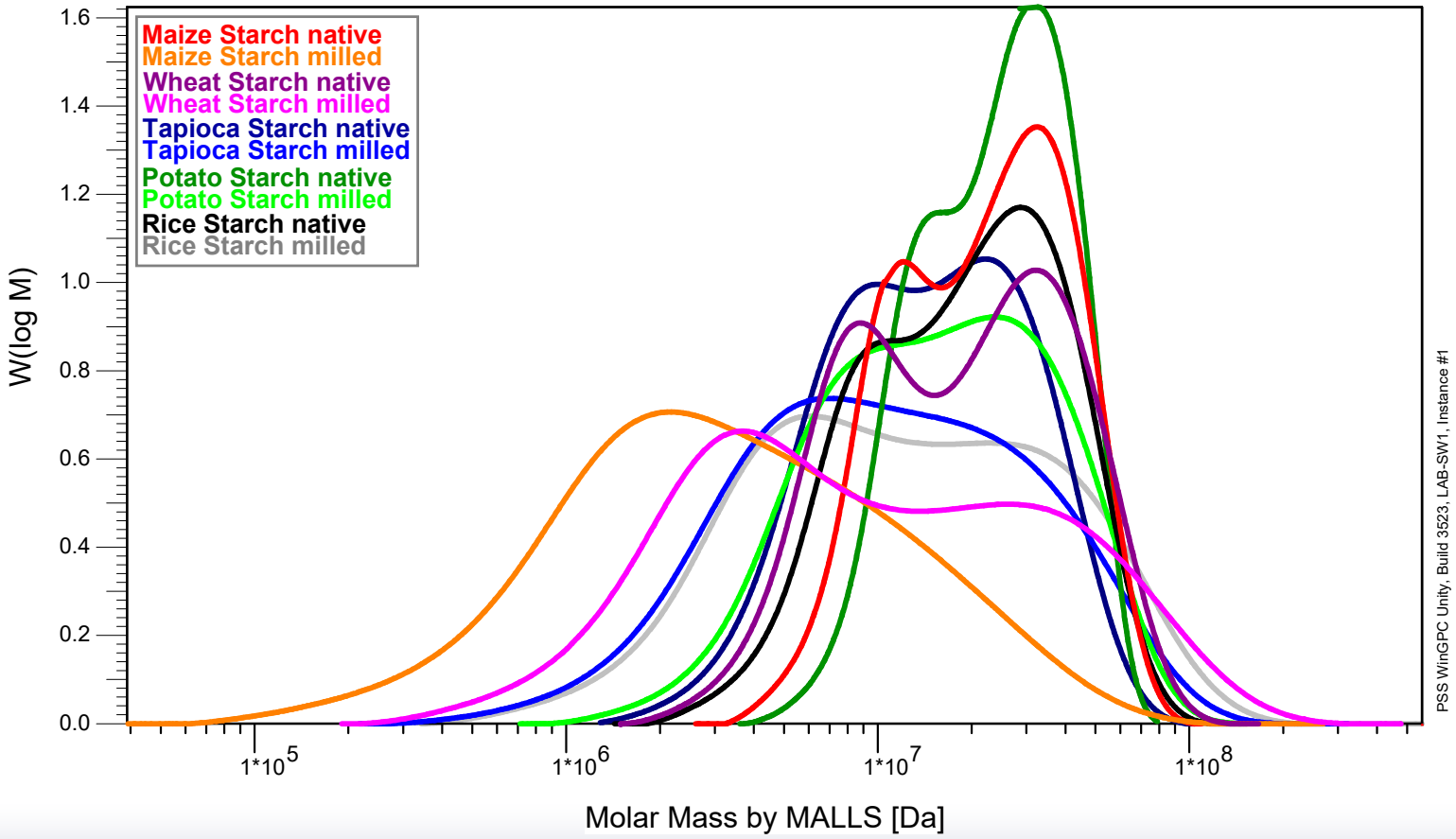
## SEC characterization of starches

SECcurity Triple system
time consuming
sample preparation

Eluent: 0.3M $NaNO_3$, pH 10
Columns:
PSS SUPREMA 20µm
Detection:
PSS SECcurity MALLS+Visco+RI
Molar masses: by SLD7000
Viscosities: by DVD1260
Concentrations: by RID

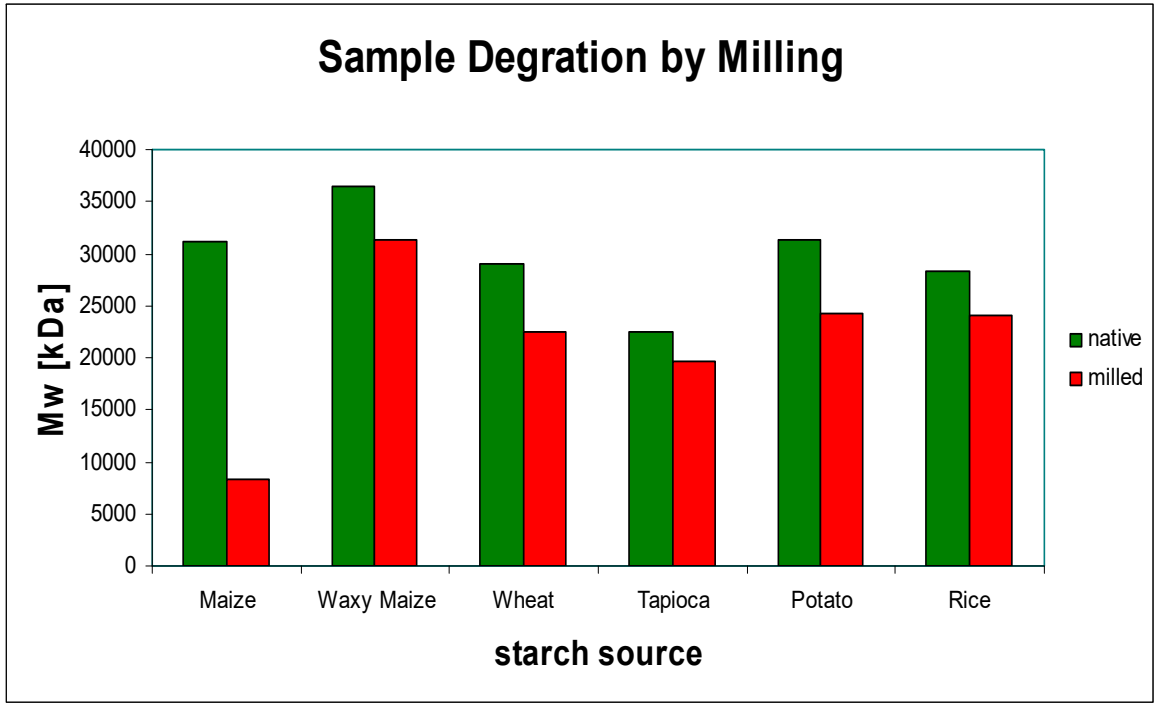


# Molar Mass Distributions native *vs.* wet-milled



# Influence of Mechanical Energy

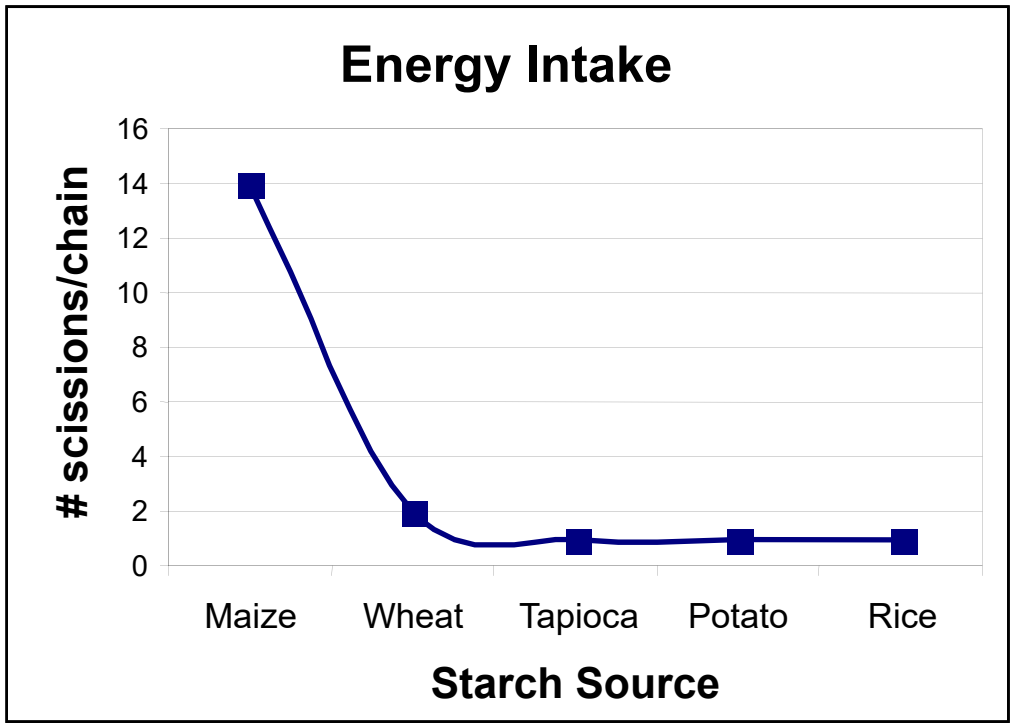
Molar mass loss: 14 – 23%
but maize: 73%




Reason?
Difference to waxy maize?

# Influence of Mechanical Energy

Determination of bond cleavages per starch chain
most varieties: 1 but maize: 14




homogeneous
energy transfer

maize different

Energy absorption and structural reasons unclear

# Starch Branching / Density Change by Mechanical Energy

$R_g$ by MALLS measures **size**

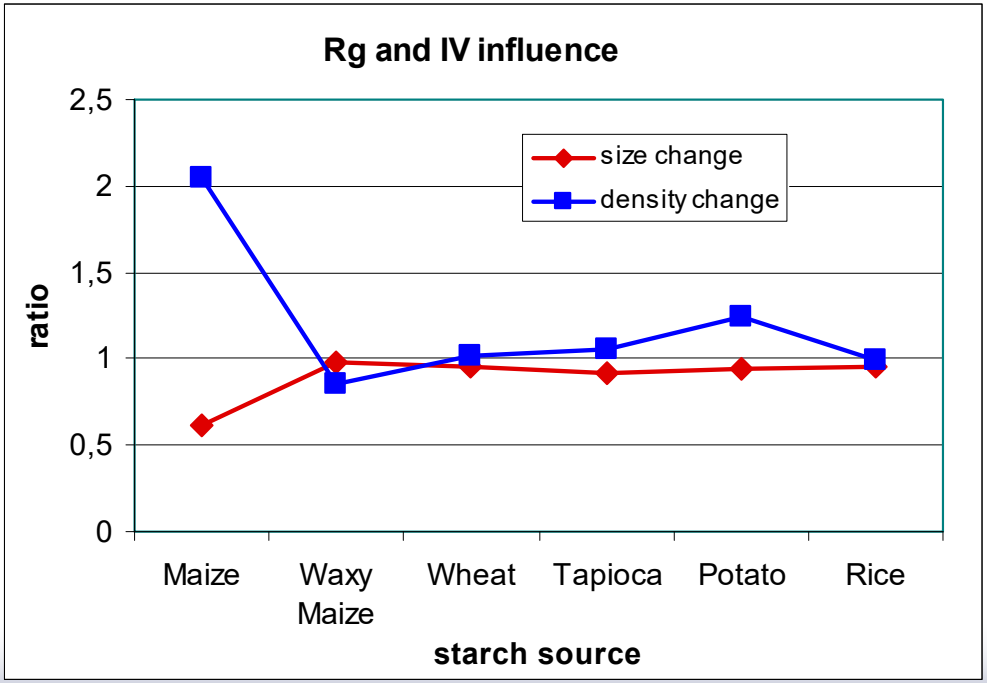
- only small variation; exception maize: 40% loss

IV by viscometry measures segment **density**

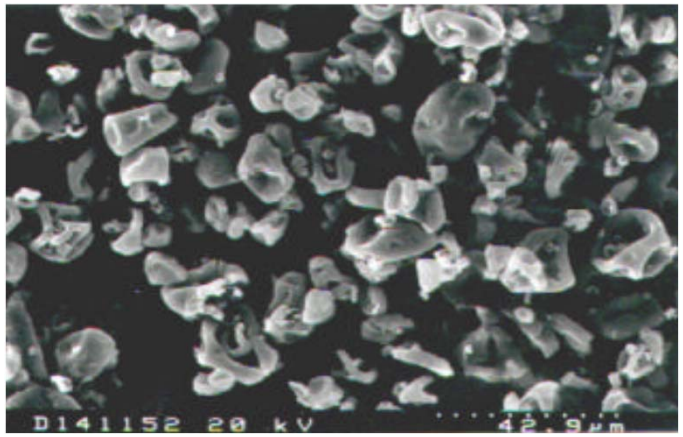
- maize starch predominantly degrades branched chains

Energy absorption:

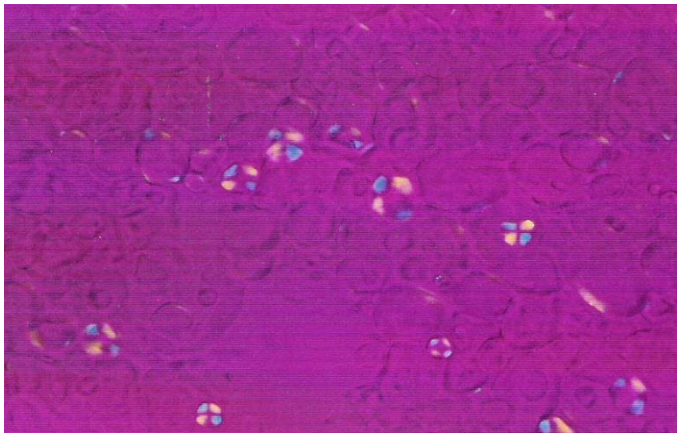
- mostly random
- BUT selective towards maize varieties



# Products Optimized by SEC characterization




water →



**spray dried starch**

**particle gels**

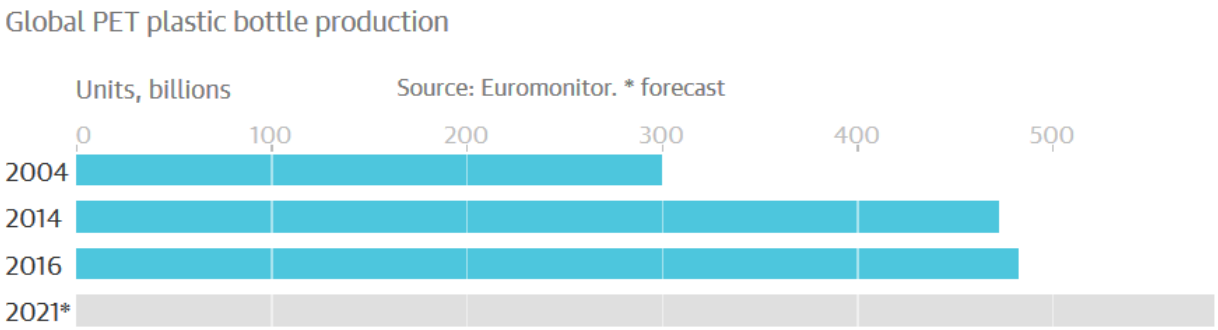
- Cereals
- Ice cream
- Ready meals, …

- Mayonnaise
- Salad dressing
- Desserts

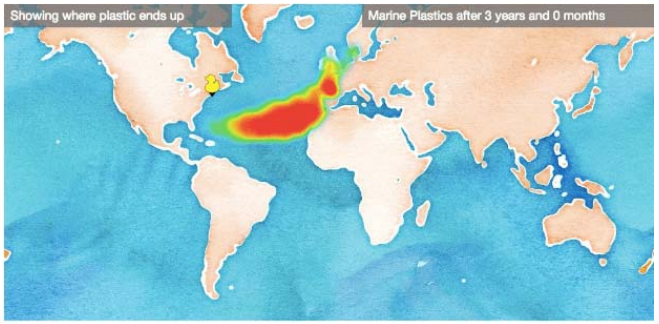
# Polymers in the Environment

## Poor Use of Plastics Pollutes Nature

- Production 2015: 320 million tons
  - >1m plastic bottles sold/min




- Most products end in landfills
- Plastics accumulate in oceans
  - → end up in human food chain



A gif taken from the website plasticadrift.org showing how plastic jetsam spreads across the Atlantic Ocean.

# Polymer Recycling

## Benefits of Polymer Product Re-use

- Reducing plastic waste
- Support sustainable environment
- Saving natural resources (oil, energy, water,…)
- Protect nature
- Prevent thermal re-use of materials


© Huffpost (2013-12-17)

# Polymer Recycling

## Problem

Reduce plastic bottle waste

µ-plastics in sea water

## Strategy

Blend recycled & virgin material

without loss of application properties

## Challenge

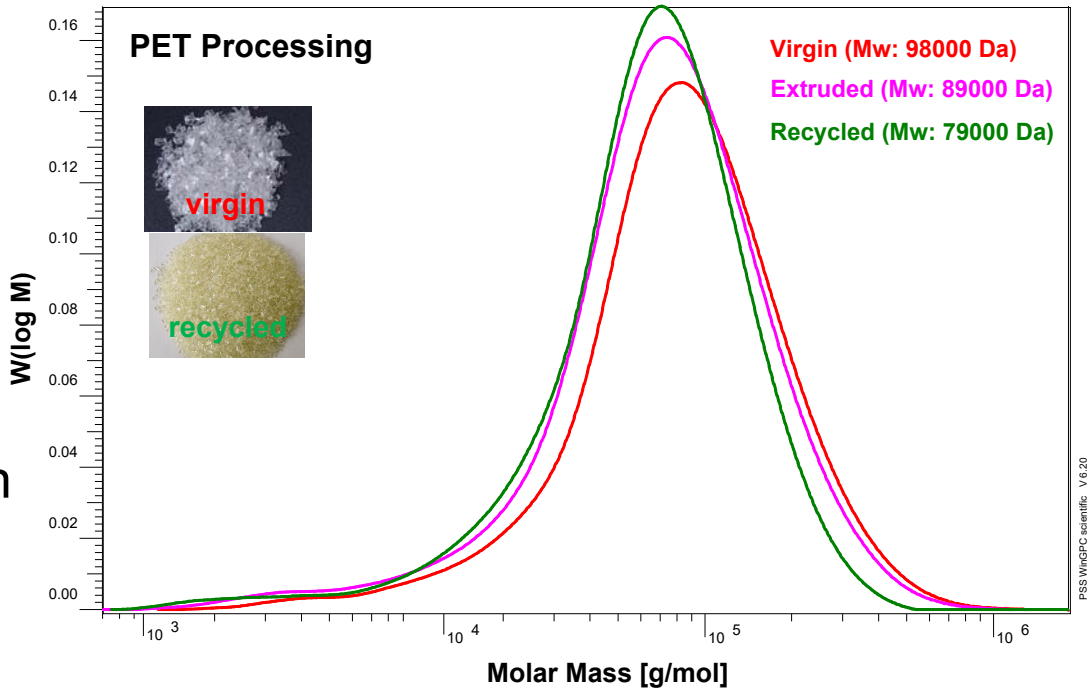
- Predict recycled material tolerated in blended product
- Correlate molecular to macroscopic properties

# PET Bottle Processing

## SEC Characterization of Products

very simple setup
high reproducability

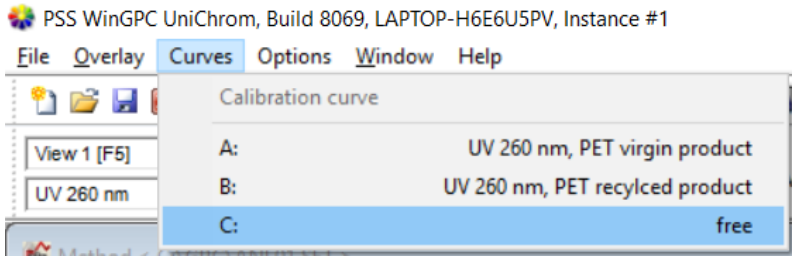
Eluent: TCM + 2%HFIP
Columns: PSS SDV 5µm
Detection:
PSS SECcurity UV & RI
Calibration: PSS PSt stds
with universal calibration
K=0.0191ml/g a=0,731
(Weiskopf,J.Polym.Sci.,A26,1919)



# PET Bottle Property Prediction

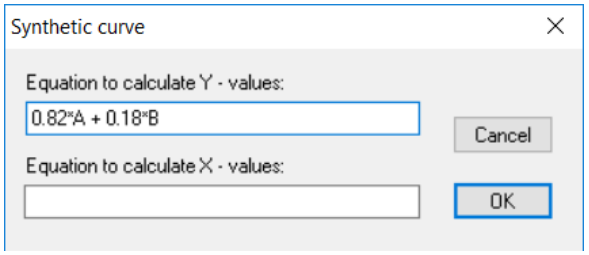
## Property Prediction/Mixing Ratio by SEC Software

1. Use SEC traces of individual products and overlay
   trace A: virgin product
   trace B: recycled product




2. Create „synthetic“ trace
   with mixing estimate

3. Enter equation of weighted
   fractions of materials:
   0.82*A + 0.18*B




4. Calculate mixed product properties

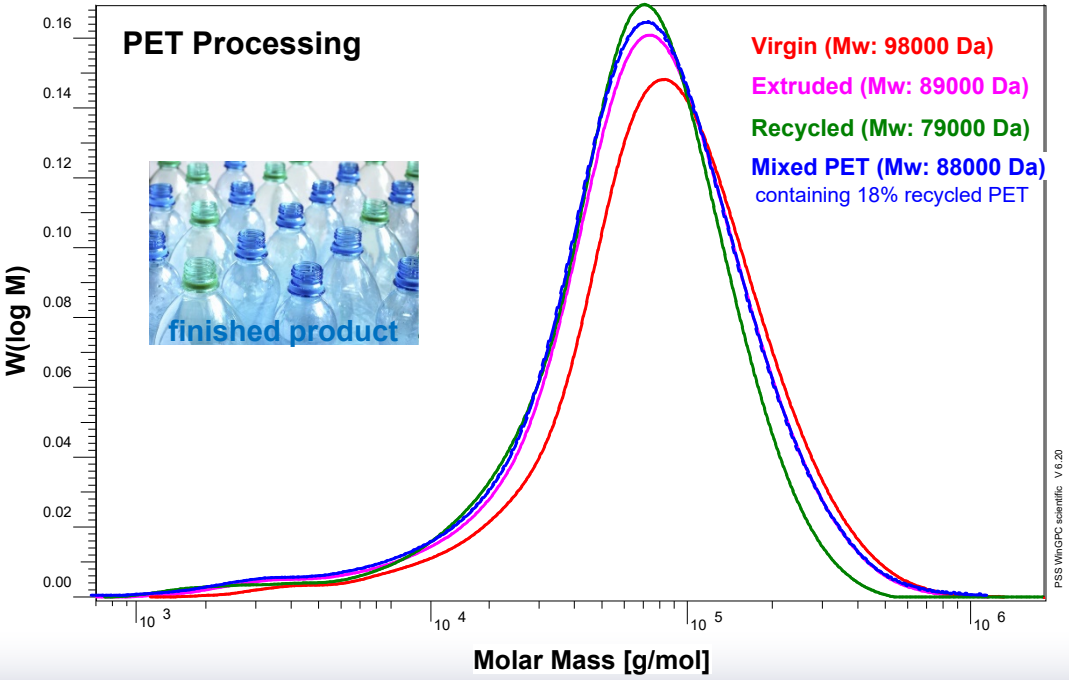
# PET Bottle Property Prediction

## Property Prediction by SEC Software

Comparison of product requirements/specs with simulation

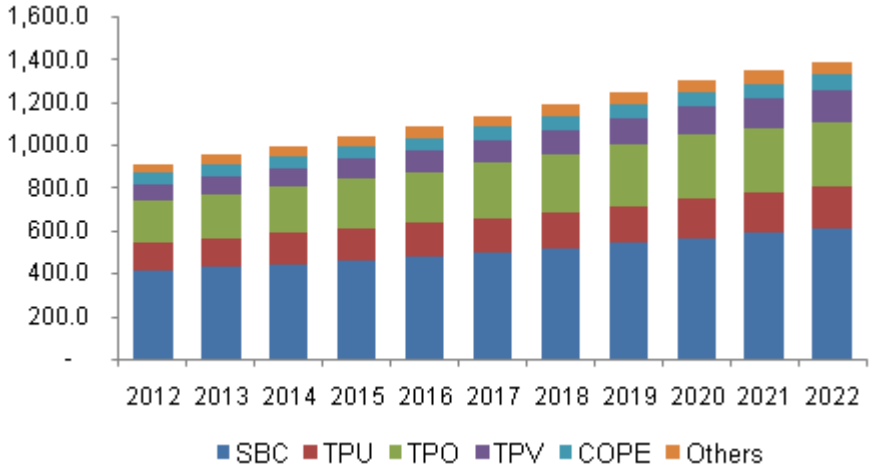
### SEC results vs. specs

| PET | IV [ml]/g | Mw [Da] |
|---|---|---|
| Virgin (this work) | 85 | 98200 |
| Extruded (this work) | 80 | 89500 |
| Recycled (this work) | 73 | 78900 |
| Regenerated (this work) | 79 | 88700 |
| Target bottle grade | 80 ± 1 | 90000 ± 2000 |
| Target film grade | 65 ± 5 | 68000 ± 2000 |
| Target fiber grade | 50 ± 10 | 47000 ± 5000 |



# Quality Assurance of TPE-s

**TPE world market (2014): 3.82 bn t/a, 16.7 billion US$**




**Advantages**:

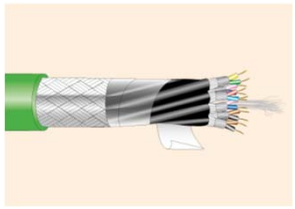
- recyclable/reusable
- similar properties as rubbers
- simple production: no vulcanization
- allows classic plastics processes (molding, extruding, etc)

# Quality Assurance of TPE-s

## Styrene block copolymer with diene-based soft segment

**Major applications/markets**

- electrical insulation



- seals / gaskets

- automotive products

- medical products

- high-toughness sports items

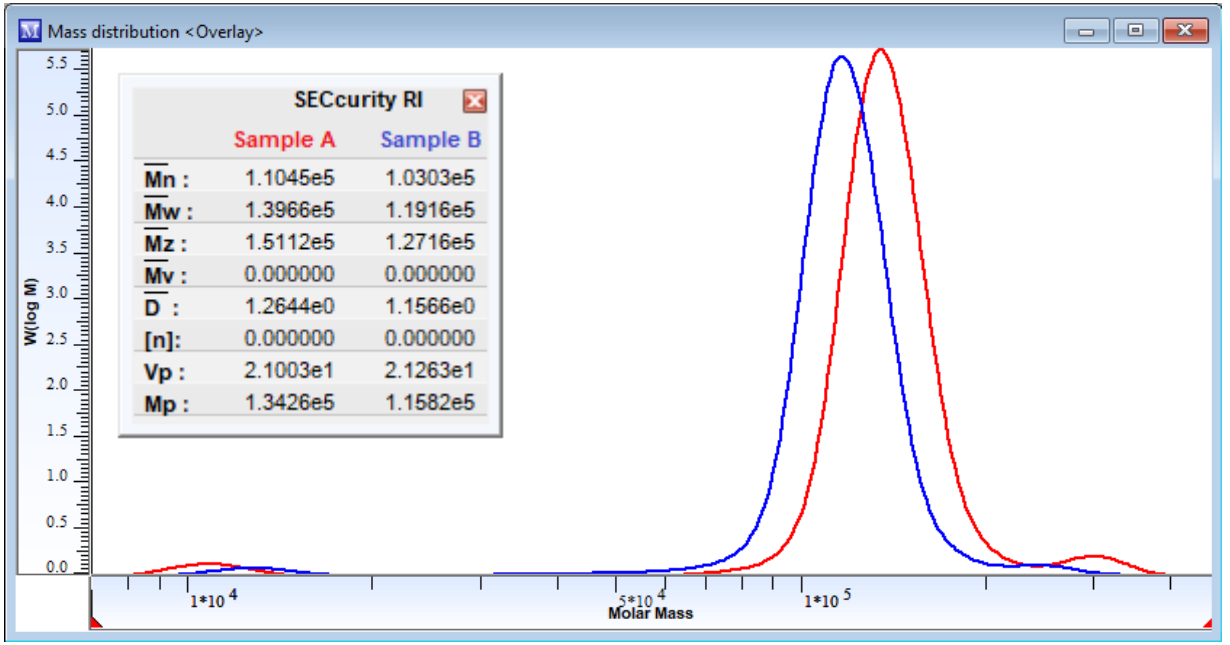
# Quality Assurance of TPE-s

## Styrene-based block copolymers – SBS type

Sample A performs according to specs
Sample B fails application tests

SECcurity system

THF @ 1ml/min
PSS SDV columns
UV/RI detection




Customer GPC/SEC results in spec and verified by PSS

# Quality Assurance of TPE-s

## Styrene-based block copolymers – SBS type

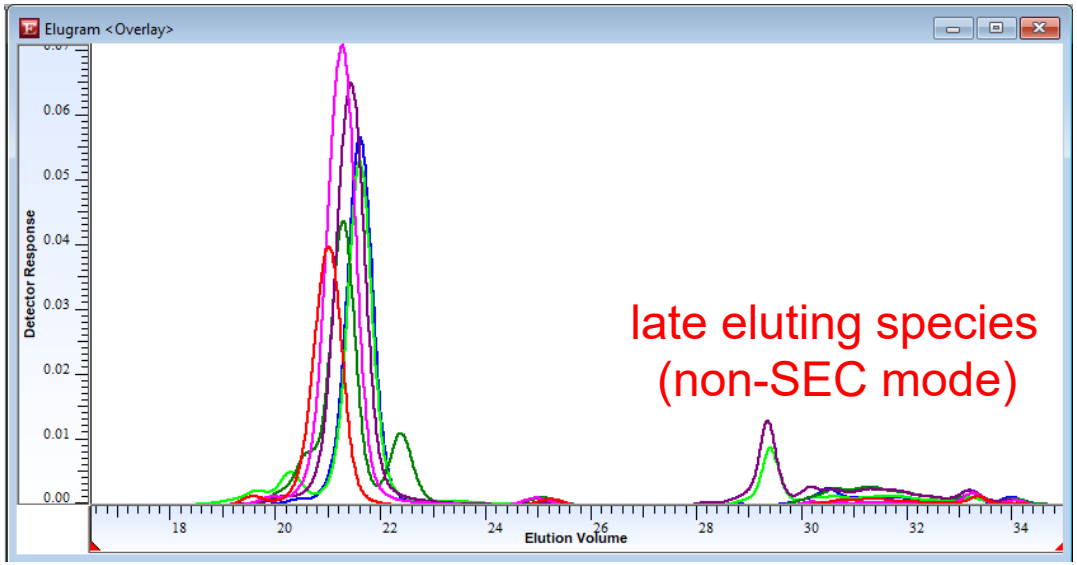
Studying product characteristics by GPC/SEC

Establishing application window

Evaluation criteria

- molar mass
- homogeneity main peak
- by products

Elucidate structure-property function relationship



# Quality Assurance of TPE-s

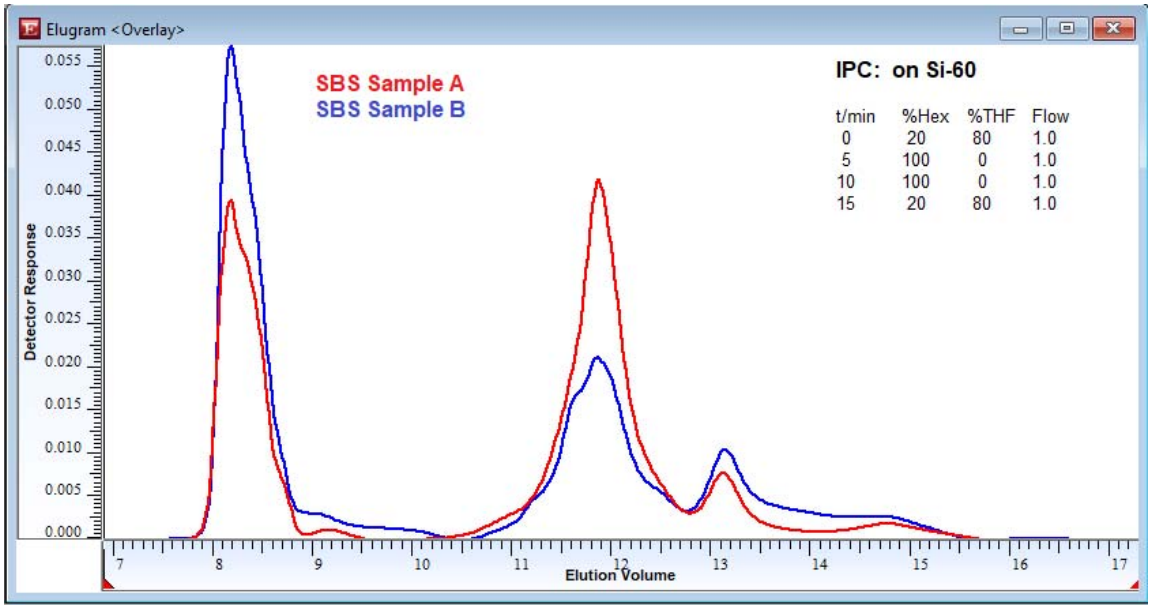
## Styrene-based block copolymers – SBS type

Good/bad product comparison by IPC

Observations:

- many peaks/components
- differences in conc.
- homogeneity unclear

*Performance difference due to composition?*

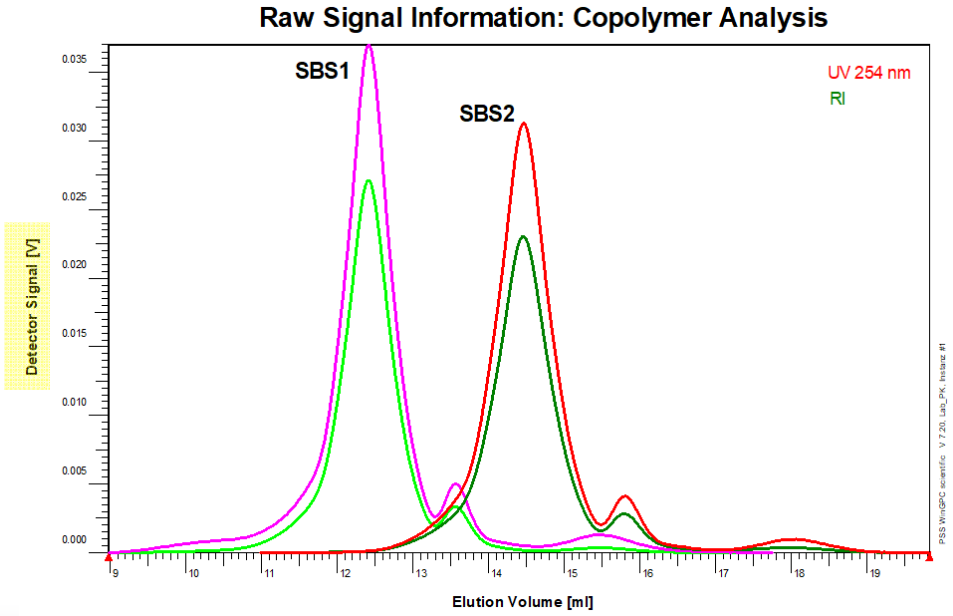


# Quality Assurance of TPE-s

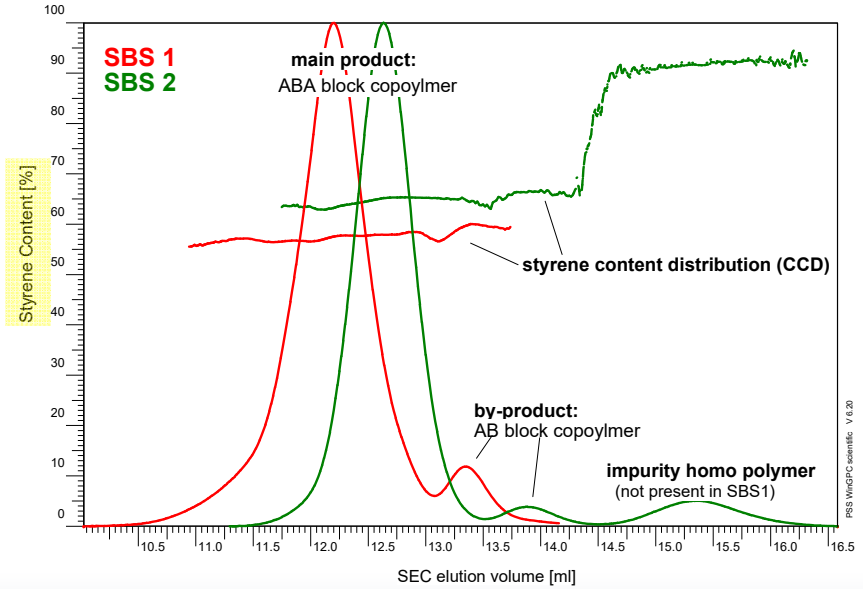
## Styrene-based block copolymers – SBS type

GPC/SEC results with multi-detection copolymer analysis

### GPC/SEC Overlay




### GPC/SEC Composition Overlay



# Quality Assurance of TPE-s

## 2-dimensional analysis for R&D

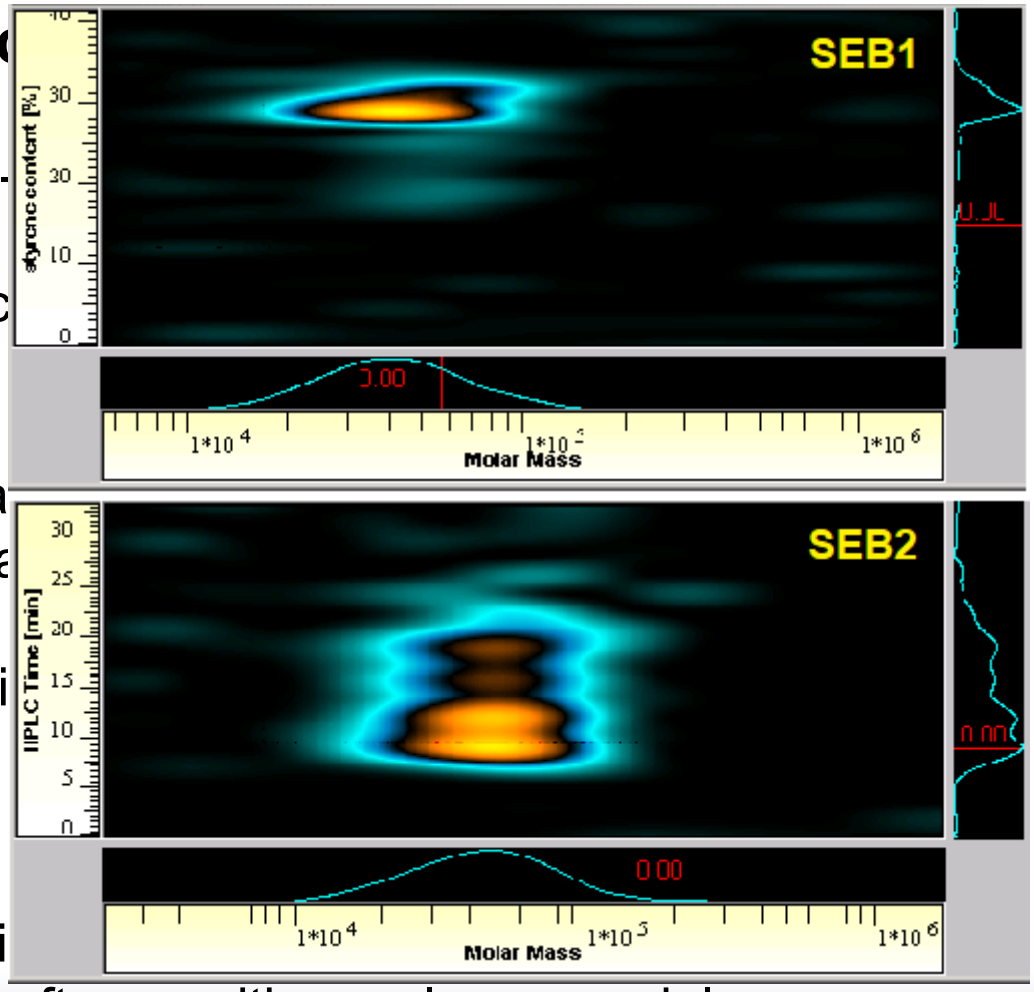
**Styrene-based block c**

GPC/SEC results with multi-

Fast screening method for c

Benefits:
- no special sample prepara
- composition results simulta
- no additional user training
- Fast analysis times (2 mi

Requirements:
- UV and RI detector
- detector response calibrati
- PSS WinGPC UniChrom software with copolymer module



# Summary

- Bottom-up product development with molecular characterization
  - has significant potential for better products in shorter time
  - supports efficient product application for best-matching markets
  - helps protecting the environment and saves natural resources
- Chromatography, esp. SEC, can play a significant role in
  - establishing structure-property-function relationships
  - investigating macromolecular properties and structural features
  - predict product properties from scaling rules
- Starch wet-milling improves food quality by
  - overcoming taste/mouth-feel issues with classical grain processing
  - prediction of sensoric behavior

- PET bottle recycling benefits from
  - optimized blending of virgin and recycled products
  - consistent product quality

- TPE product quality can be monitored by SEC
  - Molar mass distribution governs application window
  - Chemical composition distribution determines functionality

# Thank You

## Collaborators:

Prof. Claudia Niemann, HU Berlin
Prof. Robert Gilbert, U Queensland
and
PSS team

**Sprechen Sie mit uns:**

**ACHEMA 11.-15.6.2018, Frankfurt**
**Halle 4.1, Stand P48**