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# Molecular Weight Deconvolution and Chemical Composition Analysis on Complex Polyolefin Mixtures by High-Temperature GPC-IR

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# Outlines

- Introduction
  - Polyolefin structure characteristics and characterization
  - MWD deconvolution and deficiencies with GPC-DRI
  - Unique strength and excellent opportunities with GPC IR on MWD deconvolution
- Three Examples for MWD Deconvolution
  1. PE and PP “alloy”
  2. Multi-component LLDPE
  3. Impact Copolymer Polypropylene (ICP)
- Compositional Analysis for ICP Rubber Phase
  - Mathematical transformation from MW to comonomer composition (CC)
  - Results and Discussion
- Summary and Future work

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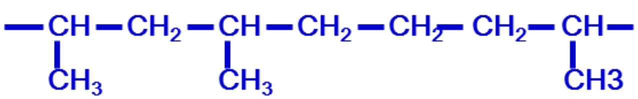
# Polyolefin System and Structure Characteristics

- **Most Versatile Material**
  - **Two elements: C and H**
  - **Broad range of properties**
  - **Broad application**
- **Heterogeneous System**
  - **Polydispersed by molecular weight**
  - **Multi-component mixture**
  - **Long Chain Branching with various architecture**



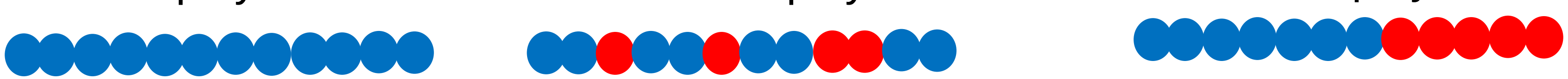

**Molecular Weight (MW)**

**Comonomer Composition (CC)**

homopolymer

random copolymer

block copolymer



**Topology**

linear

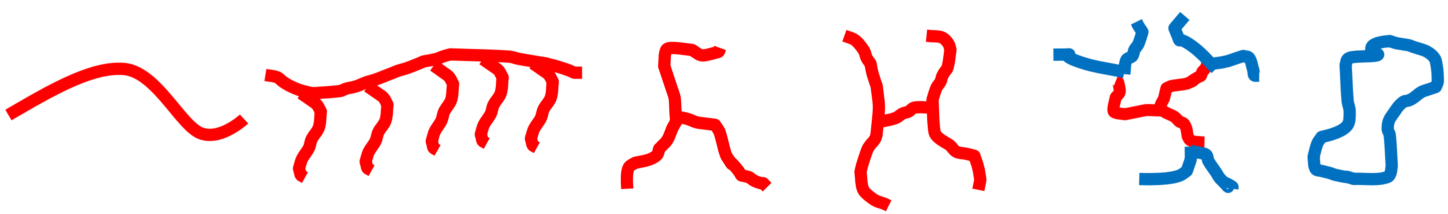
comb

star

H-shape

dentrimer

ring



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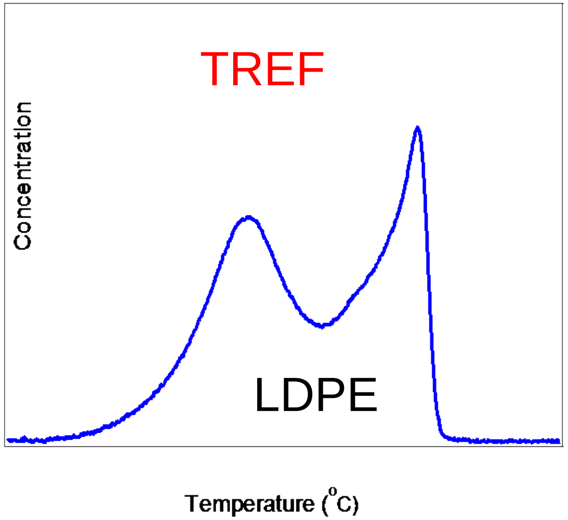
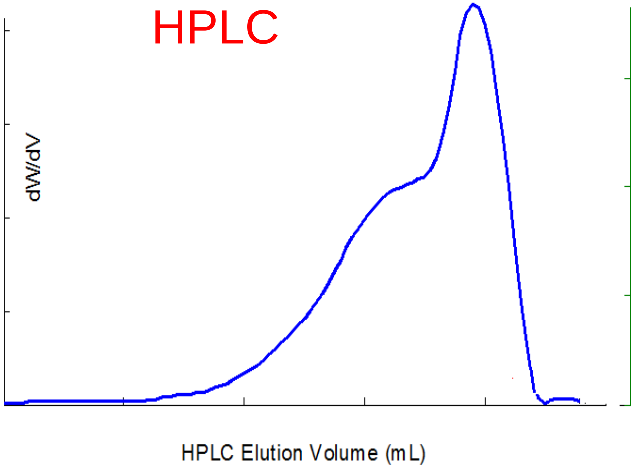
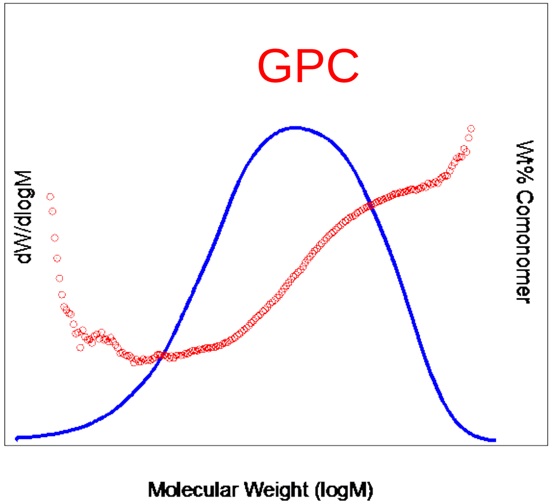
# Polyolefin Separation and Characterization

- **Polyolefin Separation**
  - **by molecular weight: GPC**
  - **by comonomer composition: TREF/HPLC**
  - **by both MW and CC (2-Dim): TREF-GPC; HPLC-GPC**




1, no amorphous phase separation
2, co-crystallization for PE and PP
3, no MW information

1, stability/reproducibility
2, separation resolution
3, multiple factors (MW, tacticity)

1, MWD usually overlap
2, no composition separation

2-Dim separation: sophisticated in operation, data processing , maintenance; time consuming

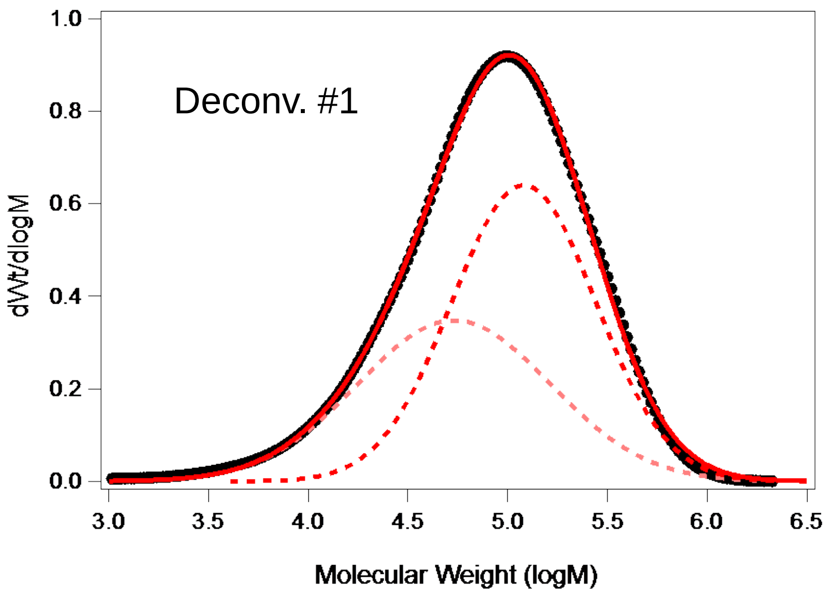
- GPC-IR: 1-dim separation with composition information; simple; fast; multi-detector hyphenation

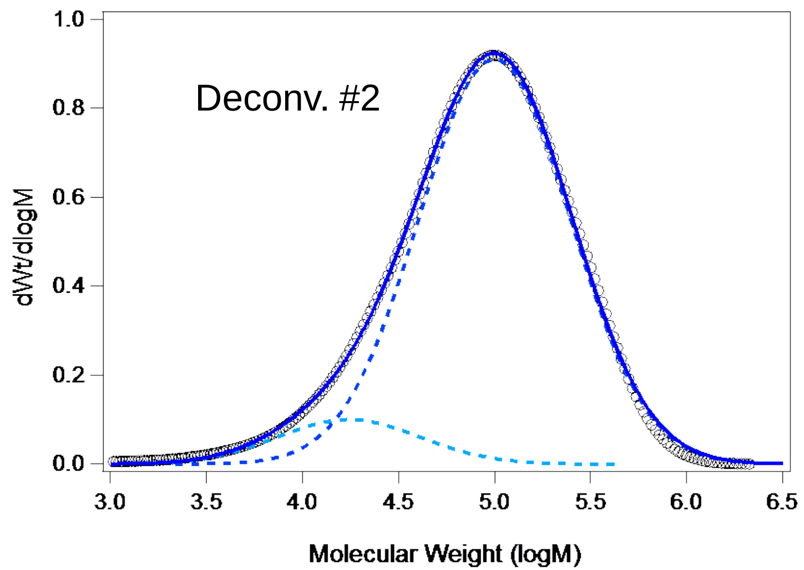
MWD deconvolution with GPC-IR

# Generally Used MWD Deconvolution Methods

- **Curve-fitting on GPC data with DRI detector**
  - **No composition information; Only MWD available**
  - **MWD deconvolution by curve fitting**
    - **function form for MWD of each component need to be known**
    - **significant uncertainty could be resulted in when MWD overlaps**

MWD Deconvolution on **same GPC MWD data (PDI~5)**
with two different combination of Gaussian functions




Two completely different deconvolution can make similar quality of fitting

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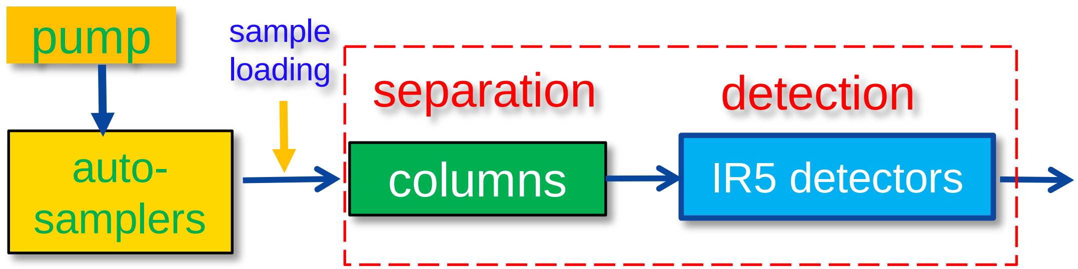
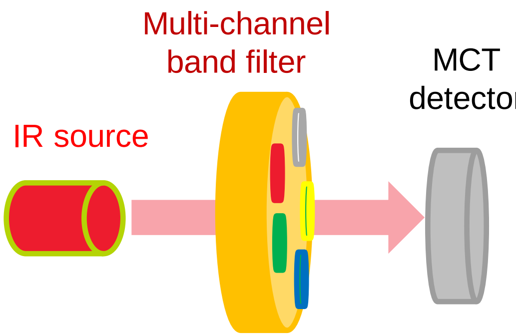
*Data were collected with ExxonMobil GPC methods;*
*Software for deconvolution: Igor Pro*

# Introduction of GPC-IR

## ➢ Schematic Diagram of GPC-IR




Schematic Diagram of Band-filter based IR detectors (IR5)




## ➢ IR5 Detector: absorbance of C-H str

- ➢ **Broad-band: 2800~3000 cm$^{-1}$;**

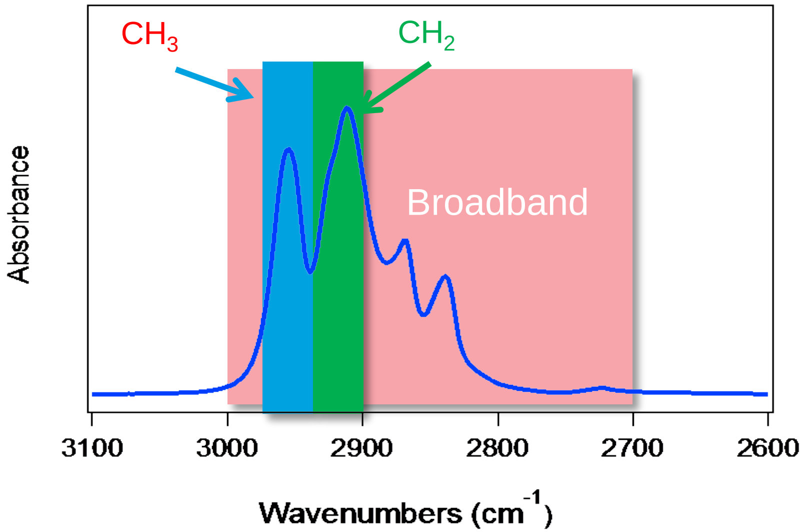
**for** **mass concentration**

- ➢ **Narrow-band: 2959 cm$^{-1}$ ($CH_3$);**

**2928 cm$^{-1}$ ($CH_2$)**

**for** **comonomer composition**

*Ortin, etc., Macromol. Symp. 2009, 282, 65–70*




** Kang, etc. Polymer 102 (2016) 99-103*

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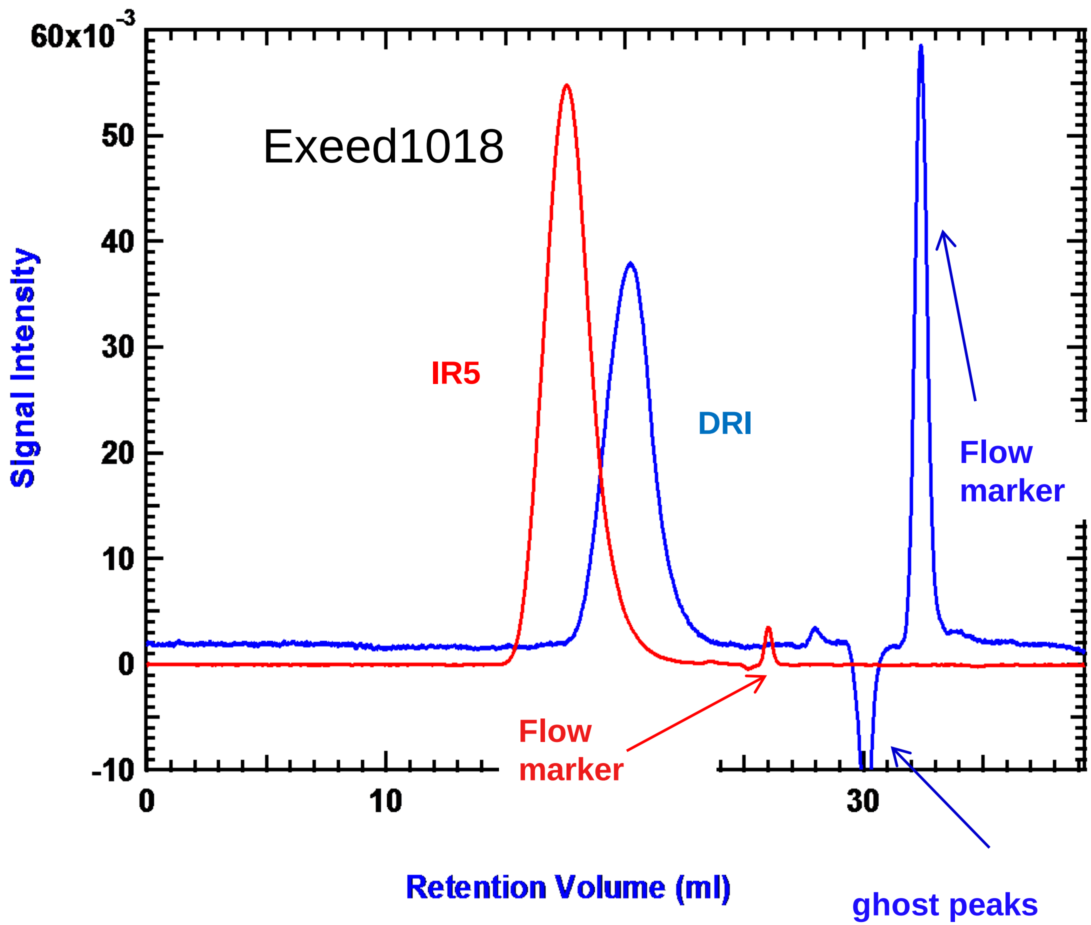
# Strength of GPC-IR over GPC-DRI: detector sensitivity

- **Response sensitivity: IR5 Vs. DRI detector**




- IR5 detector has higher S/N
- IR5 detector signal has smoother and cleaner baseline due to insensitivity to environmental change (air bubble, flow instability, pressure)
- IR5 needs less equilibration time or warm-up time (0.5 hr vs. 6 hr)

*Data were collected with ExxonMobil GPC methods*

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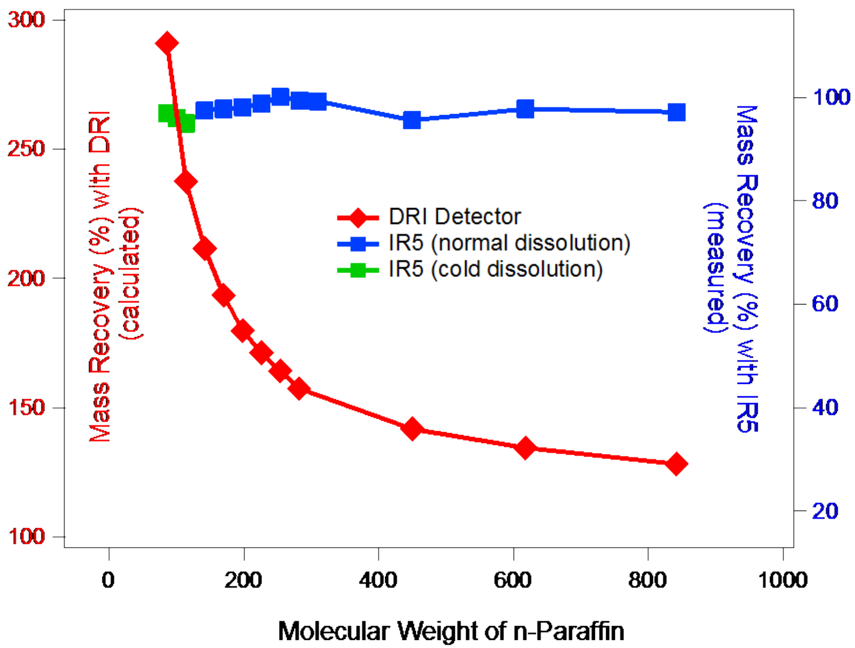
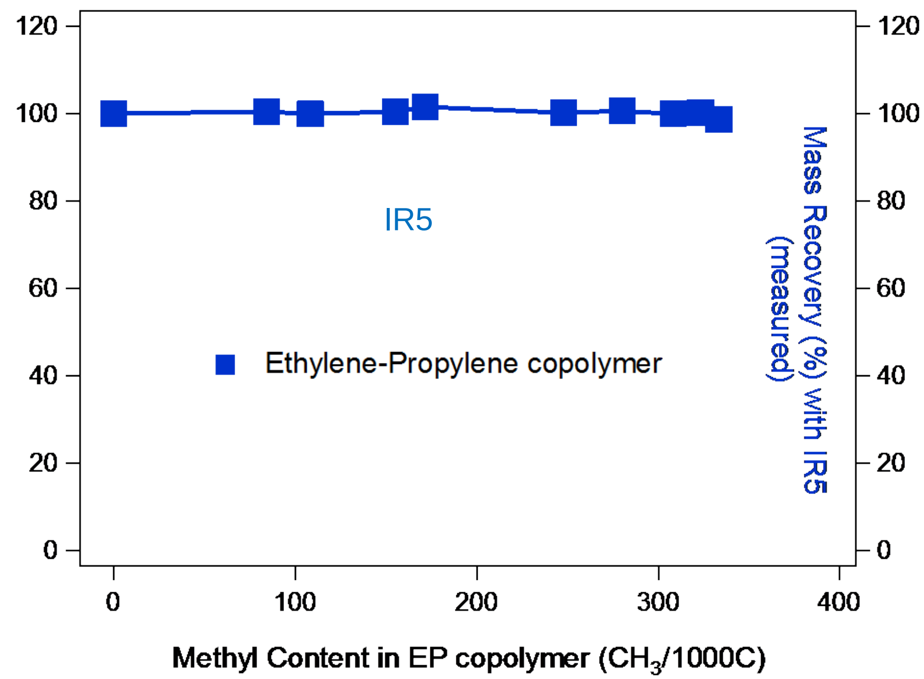
# Strength of GPC-IR over GPC-DRI: detector response linearity

- Response linearity:  IR5 Vs. DRI




*n-paraffin: purchased from Sigma-Aldrich*




- IR5 detector linearity
  - independent of MW
  - independent of composition

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*Data were collected by ExxonMobil GPC methods*

# New Approach of MWD deconvolution by adding composition constraint

- **Assumptions**
  - **Ideal elution: each component elute unperturbed**
  - **Addition rule applicable for concentration and composition**

For each elution volume slice *i*,

$$c_T^i = \sum_j c_j^i \qquad c_T^i s^i = \sum_j c_j^i s_j^i$$

- **MW calculation**
  - **Mark-Houwink equation + Universal Calibration**
  - **Empirical equation to relate comonomer composition to M-H parameters**

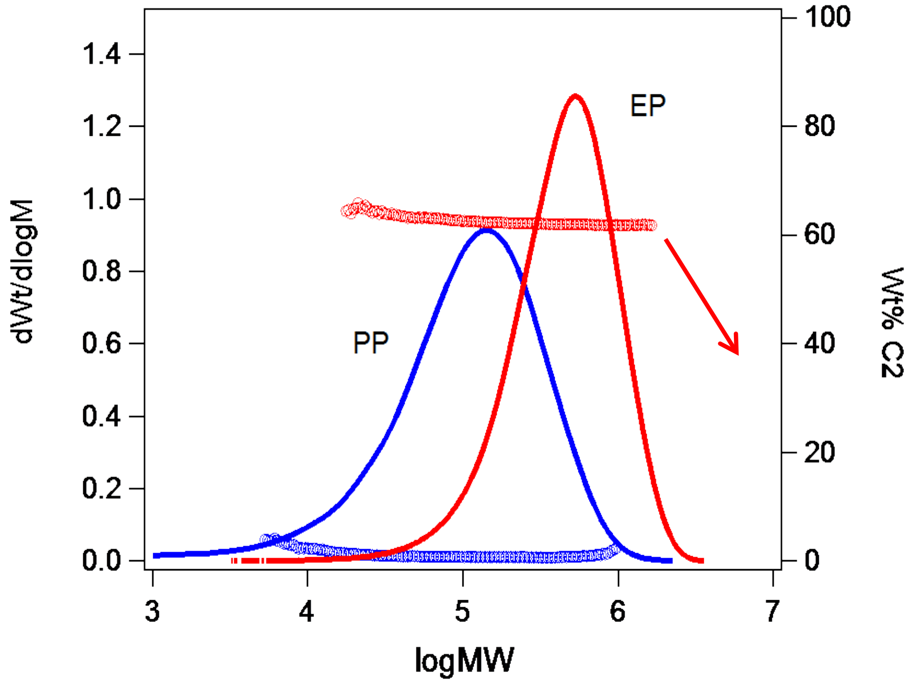
$$(K, a) \sim f(wt\%)$$

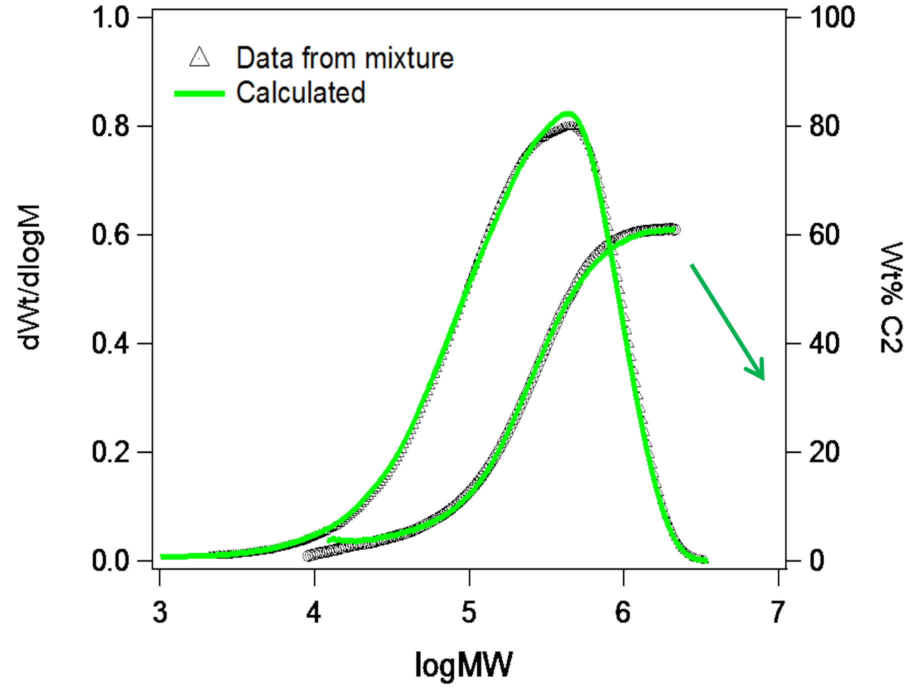
$$[\eta] = KM^a \qquad K_{PS} = 0.000175$$

$$\log M = \frac{\log(K_{PS}/K)}{a+1} + \frac{a_{PS}+1}{a+1}\log M_{PS} \qquad a_{PS} = 0.67$$

# New Approach: MWD deconvolution by adding composition constraint

- **Validation of the assumptions**
  - **Two sample mixed by given mass ratio: PP and EP**
  - **Tested with GPC-IR on the mixture and data compared with the calculated though linear combination**




*provisional patent: 2016EM110-Prov*

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# MWD Deconvolution in PE/PP mixture

- Sample: biphasic iPP-HDPE polymer granules made by series polymerization of propylene and ethylene.

- Research interest: study the growth of polymer granule so as to better understand the catalyzing mechanism

- Issue: the MWD and mass fraction for each component

For each elution slice

$$\begin{cases} c_{PE} + c_{PP} = c_T & \text{Mass conservation} \\ c_{PE}s_{PE} + c_{PP}s_{PP} = c_T s_T & \text{Comonomer conservation} \end{cases}$$

Assumed C3 comonomer content

$$s_{PE} = 0\% \qquad s_{PP} = 100\%$$

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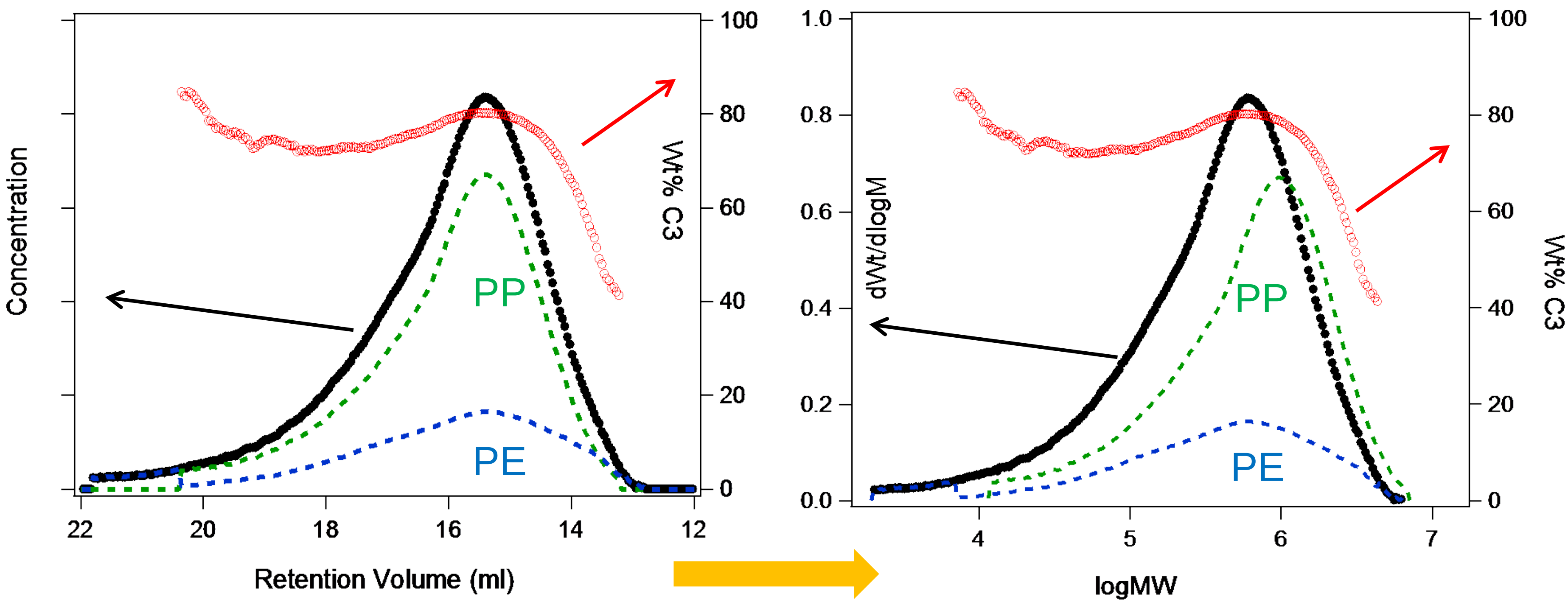
# MWD Deconvolution in PE/PP mixture

- Approach with GPC-IR:
  - PE and PP cannot be separated by GPC -4D due to overlapped MW, but can be identified by IR5 detector

Experimental condition used
dissolution: 2 hr@160C; concentration: 0.1~0.3 mg/ml; mass recovery: >80%




*Data were collected with ExxonMobil GPC methods*

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# MWD Deconvolution in PE/PP mixture

- Results and Validation by NMR

| Sample # | | Mw | PDI | Mass Fraction (GPC-IR) | Mass Fraction (NMR) | Difference GPC-NMR |
|---|---|---|---|---|---|---|
| 1 | PE | 995K | 4.7 | 46% | 48% | **-2%** |
| | PP | 1,367K | 3.9 | 54% | 52% | **2%** |
| 2 | PE | 713K | 5.2 | 26% | 25% | **1%** |
| | PP | 1,126K | 4.3 | 74% | 75% | **-1%** |
| 3 | PE | 780K | 5.6 | 66% | 66% | **0%** |
| | PP | 1,306K | 4.6 | 34% | 34% | **0%** |
| 4 | PE | 826K | 6.1 | 76% | 69% | **7%** |
| | PP | 1,046K | 5.1 | 24% | 31% | **-7%** |

*Data were collected by ExxonMobil GPC methods and analyzed with software Igor Pro*

# MWD Deconvolution for Multi-component LLDPE

- LLDPE: made from either single catalyst with two reaction sites or from two catalysts with one reaction site each

- Research interest: quantification of mass fraction, comonomer content and MW of each component (HDPE & LLDPE)

- Challenges:

$$\begin{cases} c_{HD} + c_{LD} = c_T \\ c_{HD}s_{HD} + c_{LD}s_{LD} = c_T s_T \end{cases}$$

$s_{HD}$ and $s_{LD}$ is unknown

- Two assumptions
  - low MW tail is dominated by HDPE
  - high MW tail is dominated by LDPE

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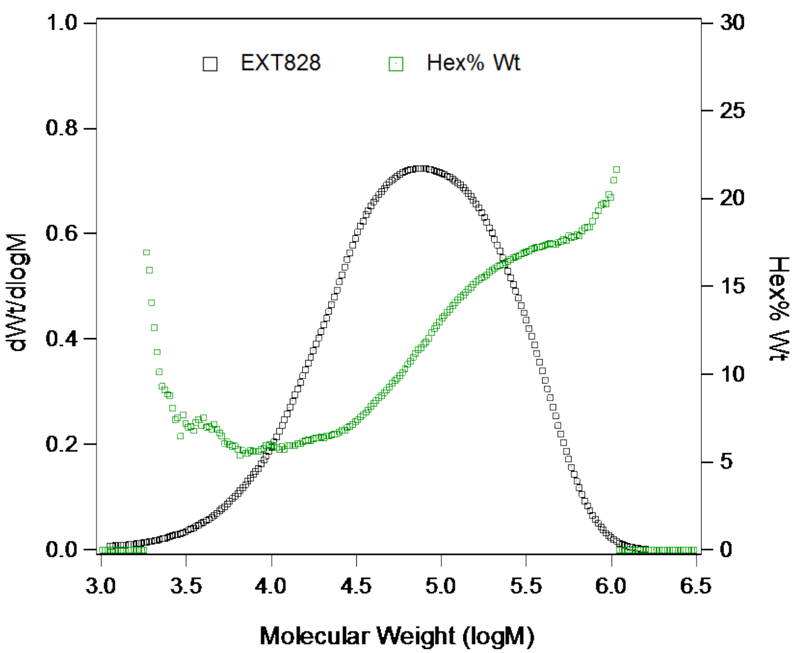
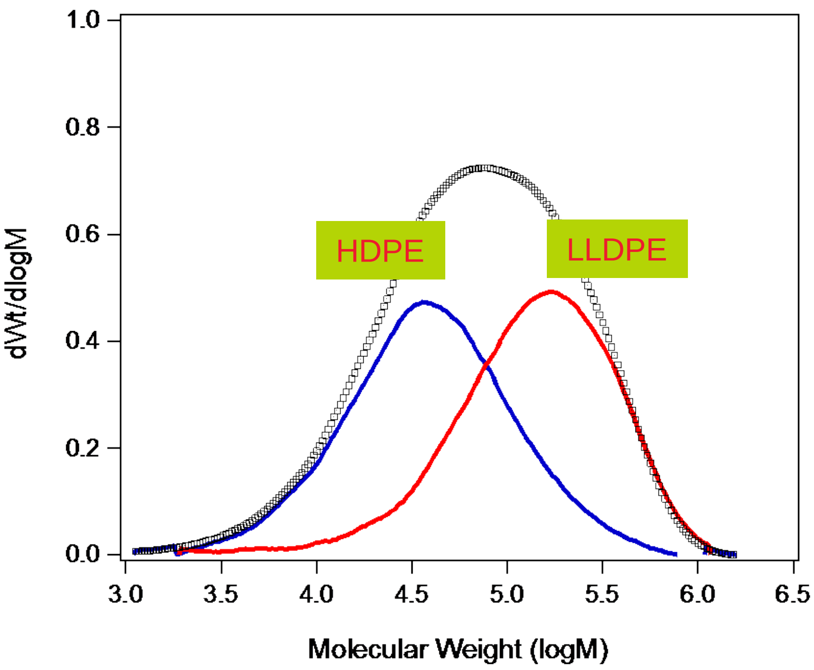
*IP.com Number: 000244739*

# MWD Deconvolution for Multi-component LLDPE

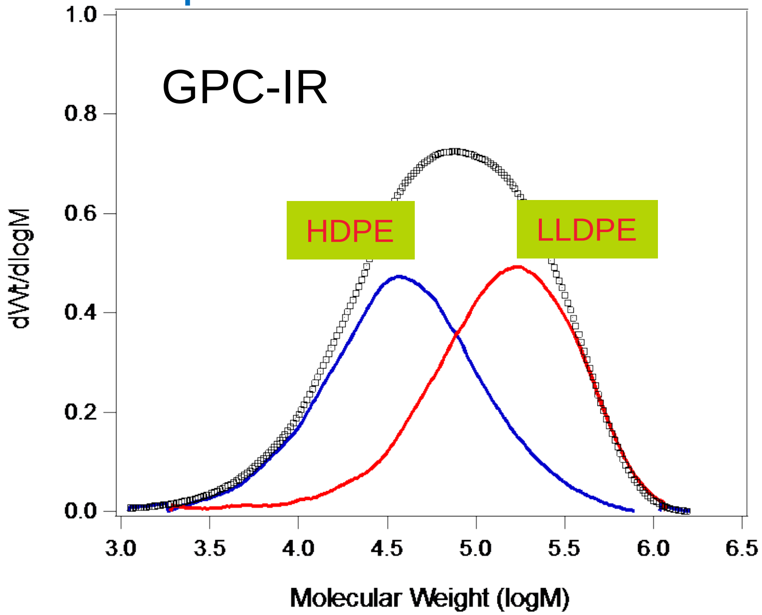
- Results from deconvolution
  - Mass fraction;  Comonomer content: Wt% C6;  MW and PDI

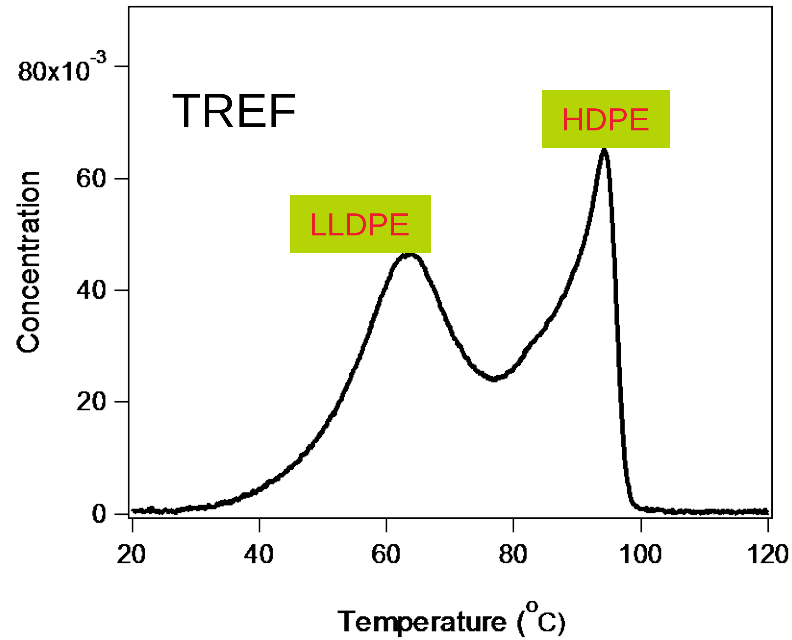


# MWD deconvolution for LLDPE

- Comparison with TREF




| | HDPE | | LLDPE | |
|---|---|---|---|---|
| | C6% or T(°C) | Mass fraction | C6% or T(°C) | Mass fraction |
| GPC | 4% | 50% | 19% | 50% |
| TREF | 94 (°C) | 45% | 64 (°C) | 55% |

# MWD Deconvolution in ICP

- ICP: a mixture of PP and EP made from two consecutive reactors.
  - PP is synthesized in the first reactor

**$C_3$= → PP**

  - EP is polymerized in the second reactor

**$C_3$= + C2= → EP**

- **Challenges for deconvolution:**
  - MW range for EP and PP are strongly overlapped
  - Total EP rubber content $R_{EP}$ and comonomer composition in EP rubber $S_{EP}$ are all unknown.

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# MWD Deconvolution in ICP

- **Methodology**
  - Concentration of EP and PP at each elution slice is related by

$$\begin{cases} c_{EP} + c_{PP} = c \\ c_{EP}s_{EP} + c_{PP}s_{PP} = cs \end{cases}$$

  - Assume the $S_{EP}$ is constant, the total rubber content $R_{EP}$ and the total comonomer content CC is related by

$$R_{EP}S_{EP} = CC$$

  - Method I: $R_{EP}$ is known from other measurement such as solid state NMR
  - Method II: PP phase (1st reactor) is available and stable in 2nd reactor

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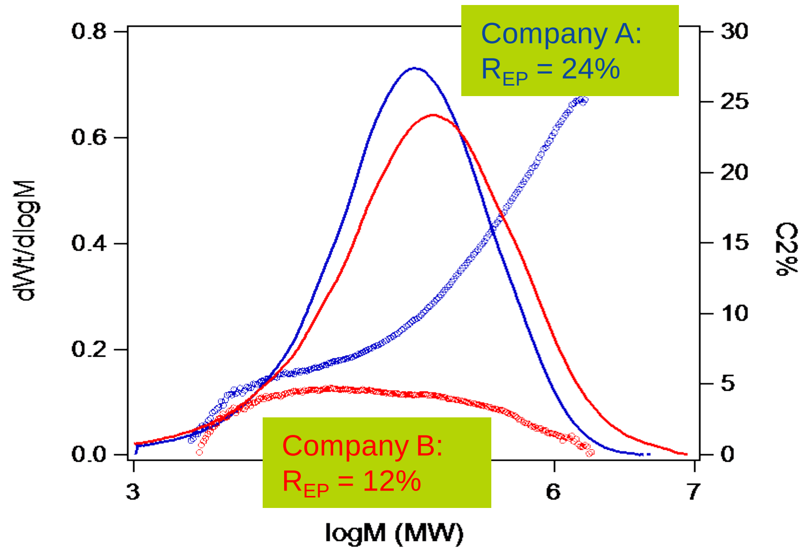
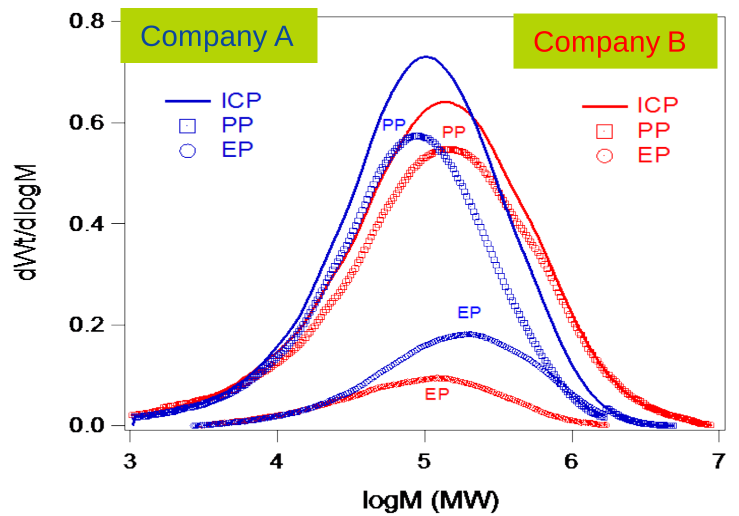
*provisional patent: 2016EM110-Prov*

# MWD Deconvolution with Method I

➢ **Method I is most applicable for analyzing commercial ICPs**




➢ The shape of “C2% vs. MW” curve reflects how the MWDs of two phases are overlaid.

“straight up”: EPR has higher MW than hPP;

“flat” EPR and hPP has similar MW;

➢ The shape of “C2% vs. MW” curve is related to the application

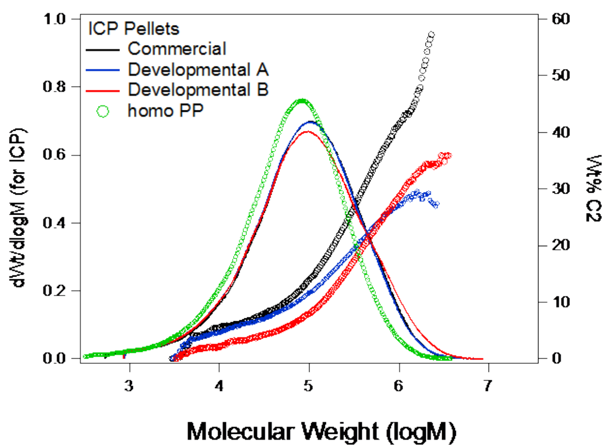
ICP with higher EP MW has higher impact strength, desirable for automotive applications

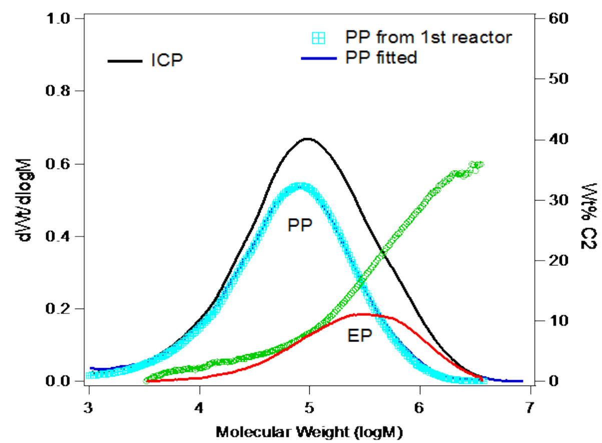
ICP with lower EP MW appropriate for high gloss small appliances.

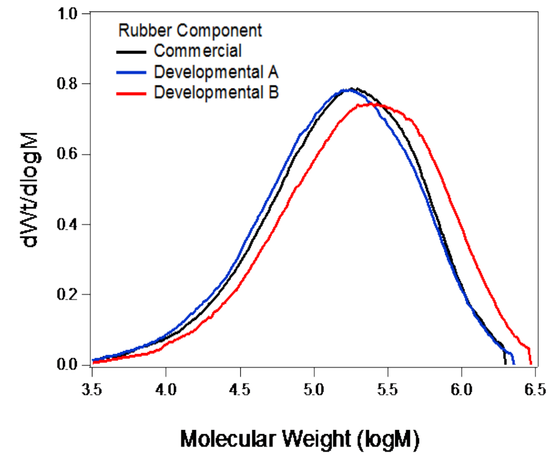
*provisional patent: 2016EM110-Prov*

# MWD Deconvolution with Method II

- **Method II is most applicable for  Research ICPs (PP phase is accessible)**




**Comparison of $R_{EP}/S_{EP}/C_2\%$ measured by current method (SS NMR+FTIR, red fonts) and GPC-IR method (green fonts)**

| Sample ID | $R_{EP}$ | $S_{EP}$ | C2% |
|---|---|---|---|
| Commercial | 26/30 | 58/55 | 15.1/16.5 |
| Developmental A | 28/29 | 42/43 | 11.5/12.3 |
| Developmental B | 25/25 | 40/42 | 10.0/10.4 |

- $R_{EP}/S_{EP}/C_2\%$ measured with GPC-IR consistent with current method
- MWD for rubber phase can be obtained

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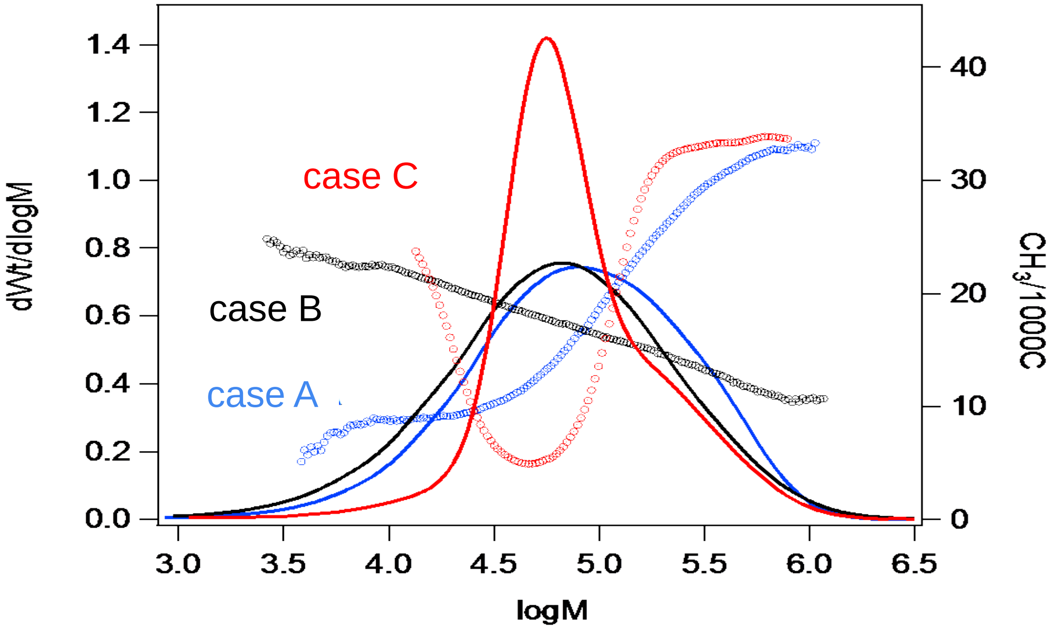
*provisional patent: 2016EM110-Prov*

# Transformation from MW into CC space about GPC-IR chromatogram

**Algorithm for chromatogram transformation from MW space to CC space (C2%)**

$$x = \log M$$

$$y = wt\%\,C2$$




$$f(y) = \begin{cases} f\big(x(y)\big)/\,y' & y' > 0 \\ -\,f\big(x(y)\big)/\,y' & y' < 0 \\ \sum_{\sec\ i} \left| f_i\big(x_i(y)\big)/\,y_i' \right| & y' < \& > 0 \end{cases}$$

**case A**

**case B**

**case C**

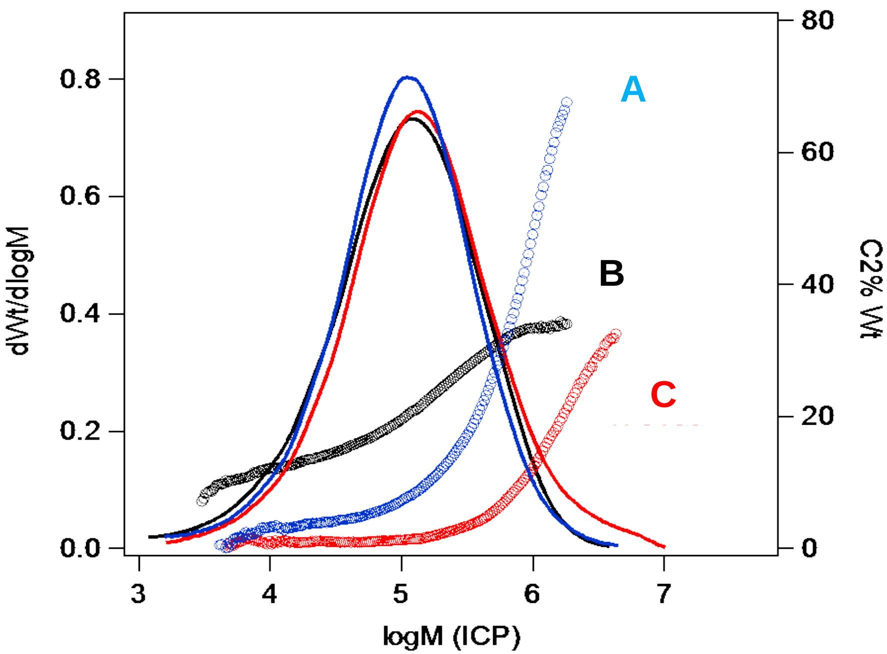


*provisional patent: 2016EM110-Prov*

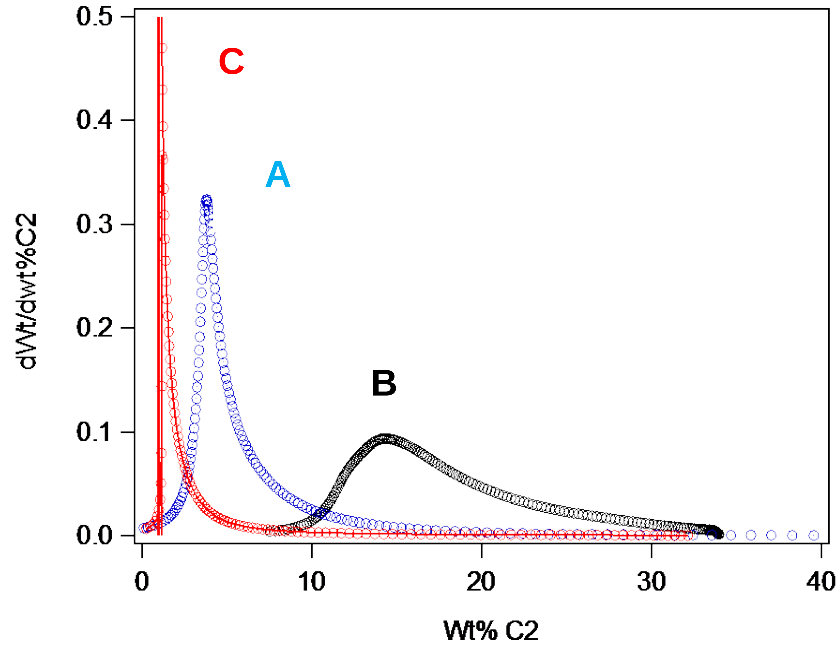
# Transformation from MW into CC space about GPC-IR chromatogram

## Three Commercial IPC samples (pellet form)

MW space




CC space




Transformation provides another facet of GPC-IR data
Features are easier to characterize (peak position, band width,..)

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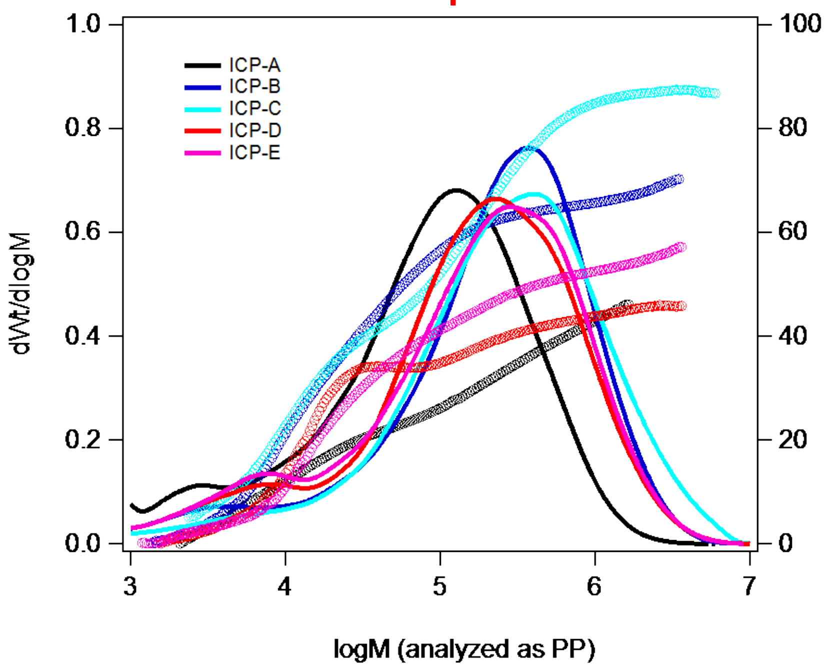
*provisional patent: 2016EM110-Prov*

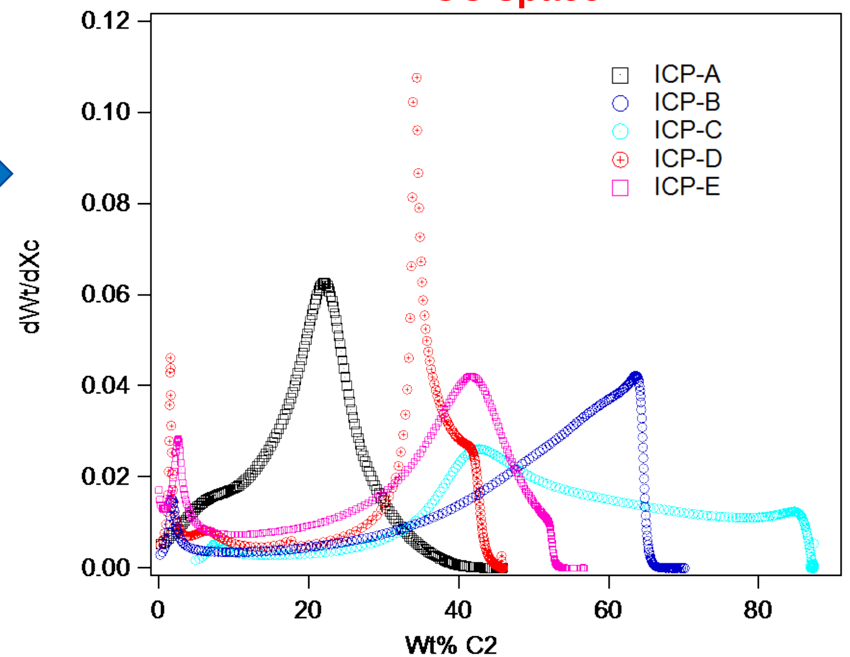
# GPC-IR Chromatogram in CC Space for ICP Rubber Phase

- **Fractionation of ICP by Xylene**
  - Reason: Rubber phase is overshadowed in CC space due to dominant PP phase.
  - Solution: PP phase can be removed by recrystallizing PP from Xylene solution. The Rubber phase sample is thus obtained by drying soluble fraction  to remove xylene

**MW space**




**CC space**




Data in CC space is more characteristic and informative

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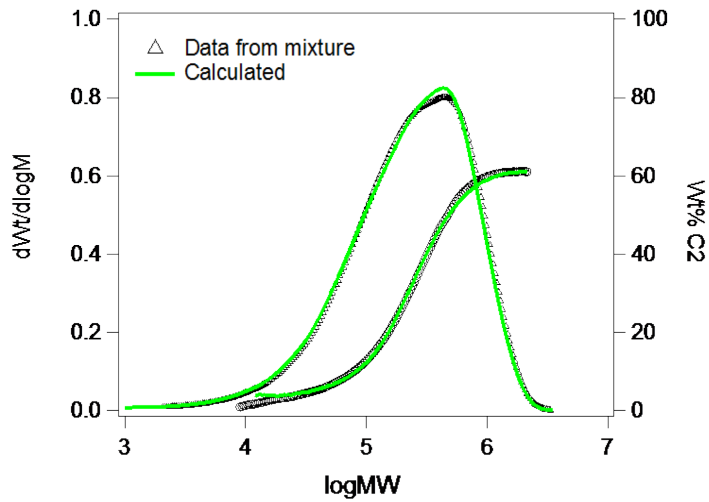
*provisional patent: 2016EM110-Prov*

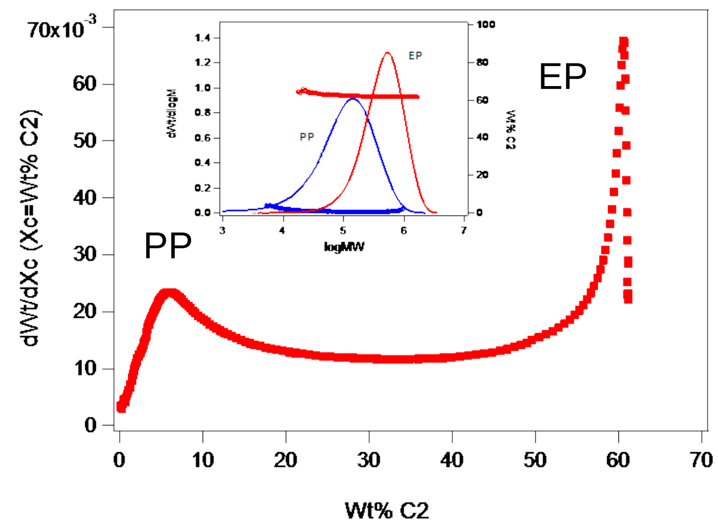
# Interpretation for GPC-IR Chromatogram in CC Space for ICP Rubber Phase

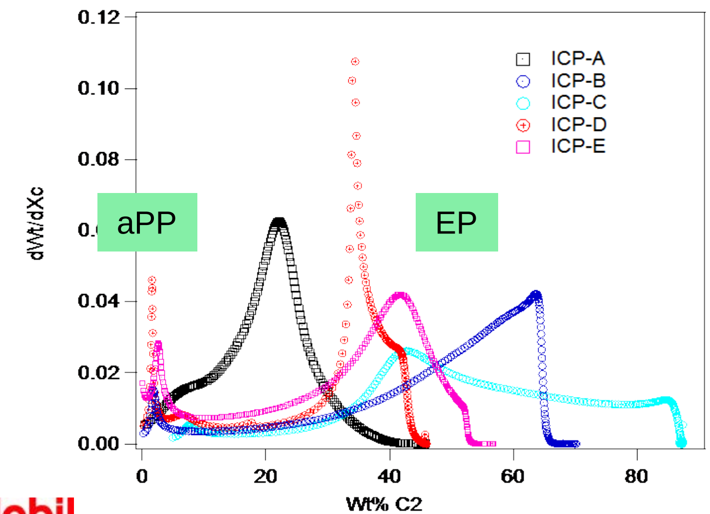
- Model mixture (EP+PP)

MW space




CC space




Sharp peak: component with certain composition

Broad peak: overlapped components

Simulation shows that the transformation can qualitatively reveal the comonomer structure of EP in ICP

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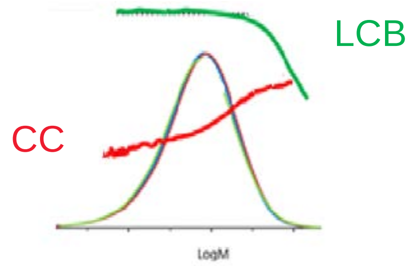
*provisional patent: 2016EM110-Prov*

# Summary

- Polyolefin is a complicated multi-component system while the MWD deconvolution for each component is very important for research
- Compared with traditional GPC (DRI based), the extra detection on comonomer composition in GPC-IR technique provides excellent opportunities for new method development on MWD deconvolution, which does not need the assumption about the MWD function of individual component.
- A series of deconvolution methods have been developed and applied in different polyolefin system: PE/PP “alloy”, LLDPE, ICP.
- A transformation of GPC-IR chromatogram from MW space to comonomer composition space provides a qualitative information on the structure of ethylene-propylene rubber in ICP.
- Challenge in future: Deconvolution on LCB?

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