

Characterization of Chemical Composition Heterogeneity and its Correlation to Molecular Weight in Polyolefin Copolymers

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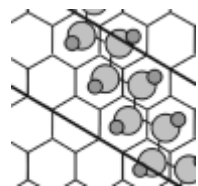
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- 1. Separation of non-crystalline polyolefins based on chemical composition;**
- 2. A quantitative determination of the concentrations of the separated fractions;**
- 3. A strategy to determine compositions of the separated fractions.**

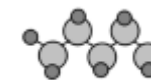
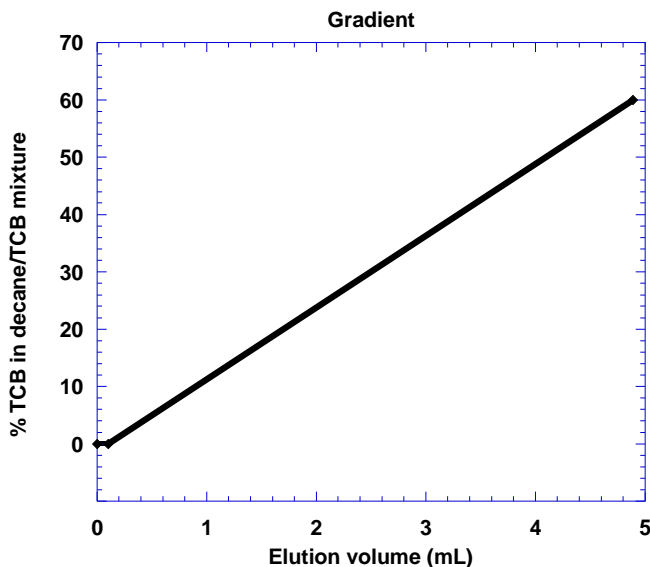
Separation Technique: Adsorption HTLC



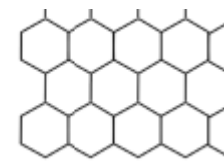
Temperature = 140 °C:
Sample is above its crystallization temperature through the separation process



Polyolefin adsorbed on graphite in decane



trichlorobenzene/decane

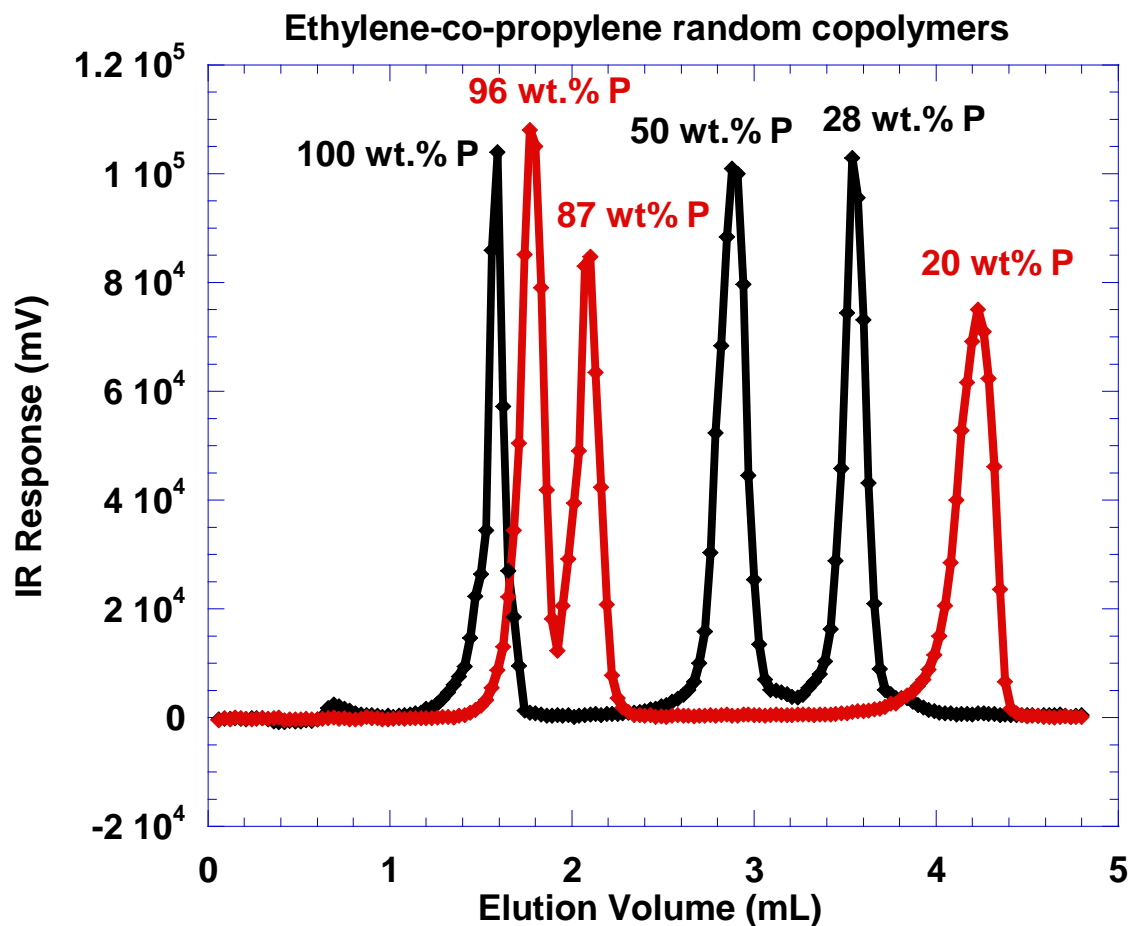


Polyolefin desorbed from graphite in high content of TCB

Polyolefin with higher ethylene content has higher affinity with graphite. It requires more TCB to be desorbed. Separation was achieved by changing the TCB content in the mobile phase.

Picture of adsorption of alkanes on graphite was from Phys. Chem. Chem. Phys. 2002, 4, 345, by Arnold T. et. al.

Separation by Chemical Composition



Wt % P is weight percentage of propylene in the polymer, determined by NMR.

Amorphous and semi-crystalline samples were separated by their chemical compositions.

Quantification by IR Detector

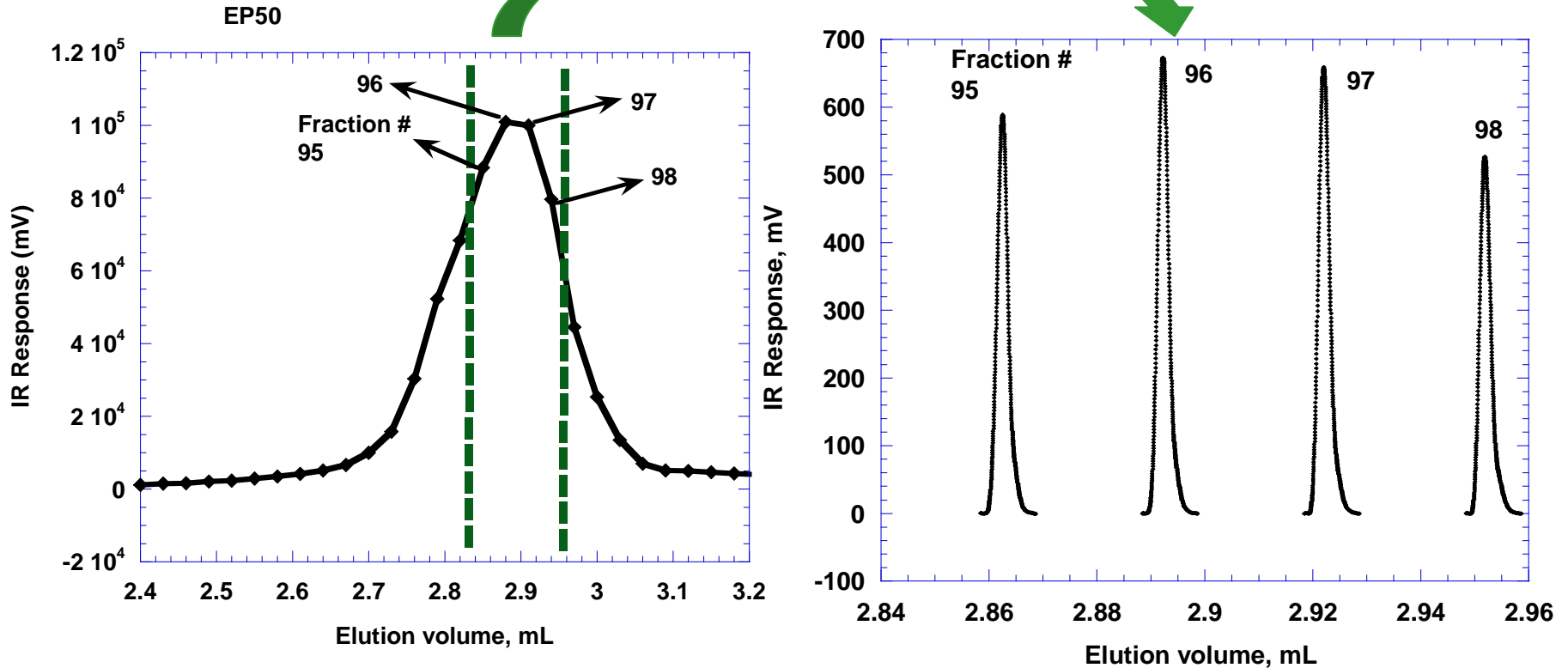


	Sample Preparation			IR Detection		area% - wt%
	Sample	Mass (g)	wt%	IR area (mV)	area %	
Blend 1	iPP	0.0114	28.4	4.52×10^5	26.2	-2.2
	EP50	0.0161	40.0	7.00×10^5	40.1	0.1
	EP28	0.0127	31.6	5.90×10^5	33.8	2.2
Blend 2	EP96	0.0127	34.2	5.86×10^5	35.0	0.8
	EP87	0.0109	29.4	4.50×10^5	26.7	-2.7
	EP20	0.0135	36.4	6.46×10^5	38.3	1.9



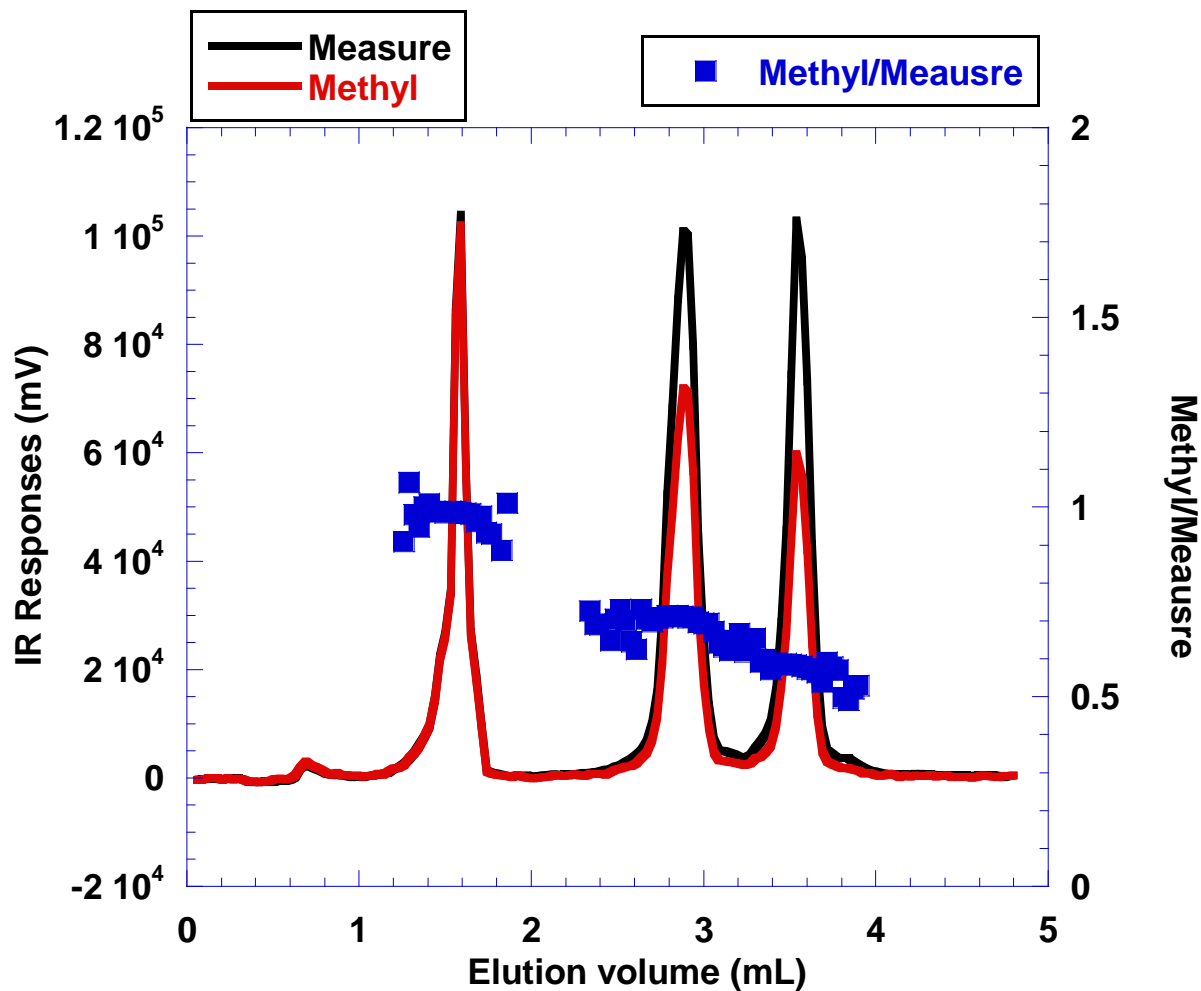
Good estimation of the concentrations of the components in the blends.

Adsorption HTLC x SEC-IR



Every 30- μ L cut was taken from HPLC eluent and the cut was analyzed by SEC-IR. The use of SEC allowed using infrared absorbance detector (IR) for quantitation.

Determine Chemical Composition by IR

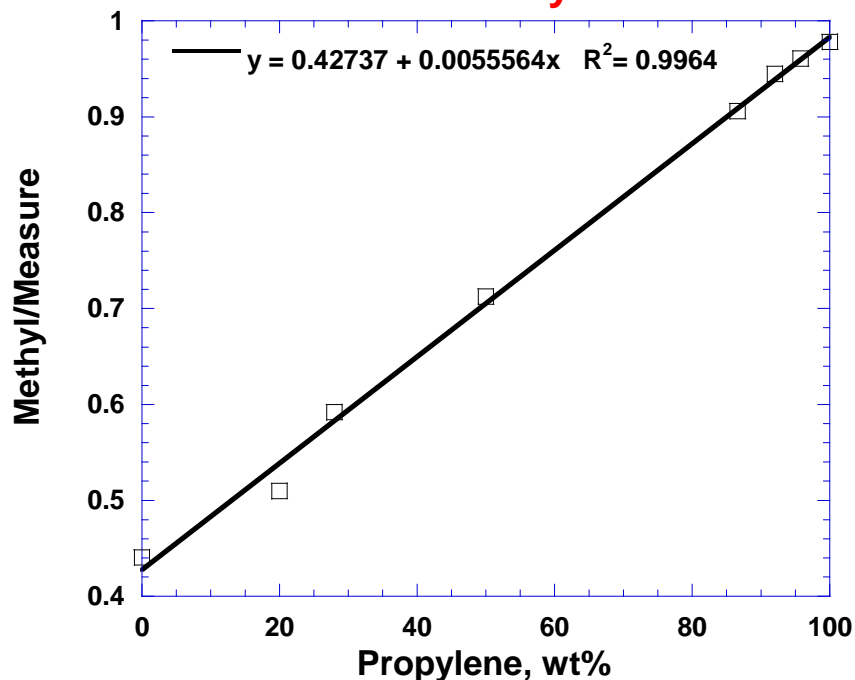


The use of concentration band (“measure”) and composition band (“methyl”) is for determining compositions of the separated fractions.

Chemical Compositions of Components



Calibration curve by SEC-IR



	wt% P	wt.% P from Calibration	wt% P difference
	NMR	IR	IR - NMR
iPP	100	101	1
EP50	50.0	50.3	0.3
EP28	28.0	28.8	0.8

IR methyl/measure ratio can be used to determine the chemical composition of the separated fractions.

Requirements to obtain CCD of polyolefins:

1. Separation of non-crystalline polyolefins based on chemical composition ;



2. A quantitative determination of the concentrations of the separated fractions;



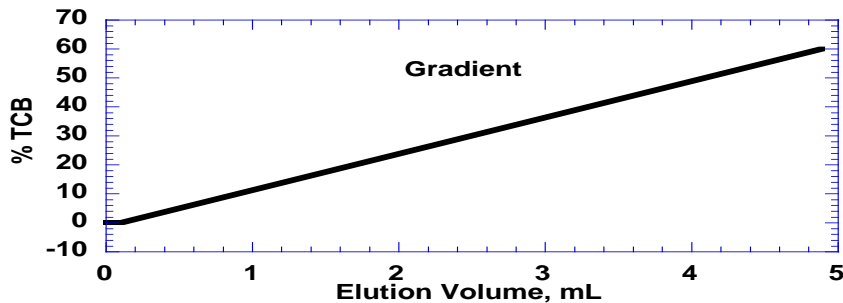
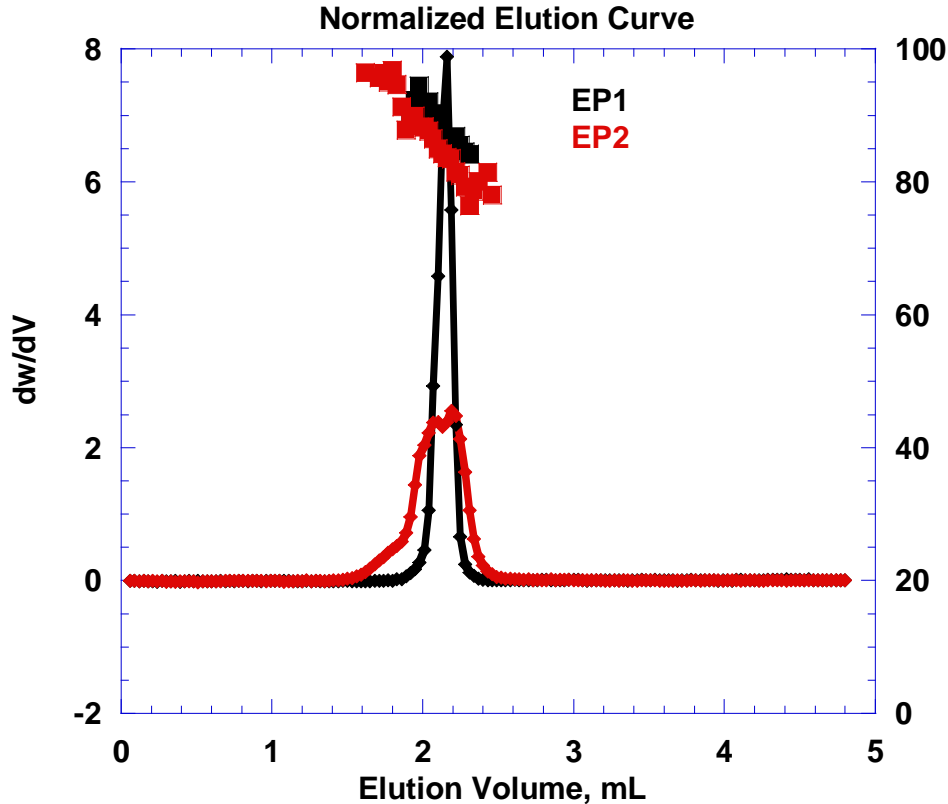
3. A strategy to determine compositions of the separated fractions.



All requirements were met.

Next: Derive a metric to represent the breadth of CCD.....

Two EP Copolymers



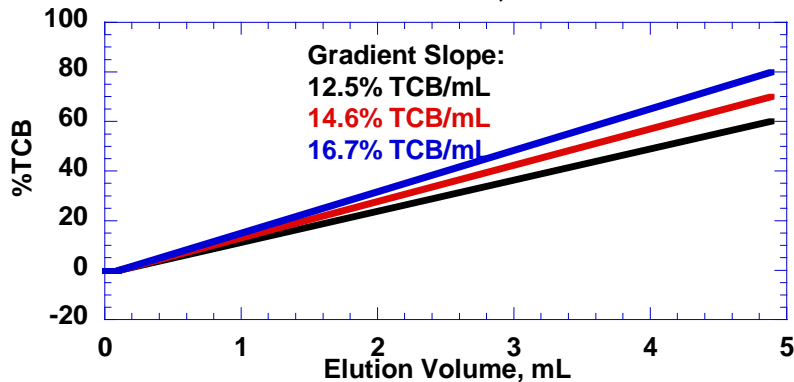
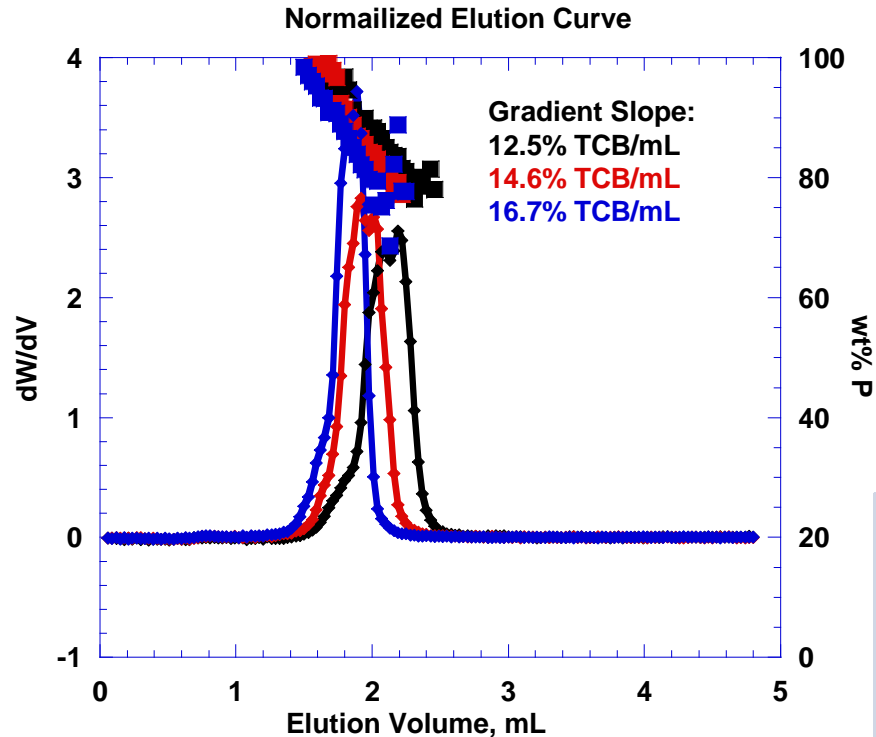
Tentative metric for CCD breadth

	wt% P	wt%P (25%, high) - wt%P (25%, low)
	average	
EP1	87.7	4.9
EP2	85.6	11.7

Wt%P (25%, high) is the composition of 25% of the fractions with highest propylene content.

Wt%P (25%, low) is the composition of 25% of the fractions with lowest propylene contents.

Gradient Impact on EP2



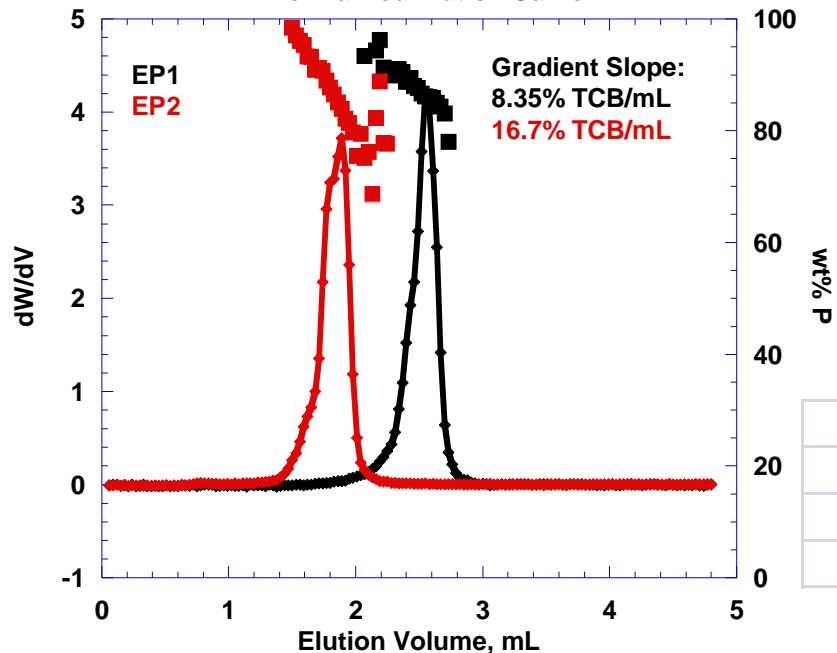
Gradient % TCB/mL	wt% P average	wt%P (25%, high) - wt%P (25%, low)
12.5	85.6	11.7
14.6	87.0	12.3
16.7	86.8	11.5

1. Gradient changes the slope of wt%P – elution volume.
2. Wt%P (25%, high)-wt%P (25%, low) is independent from the gradient.

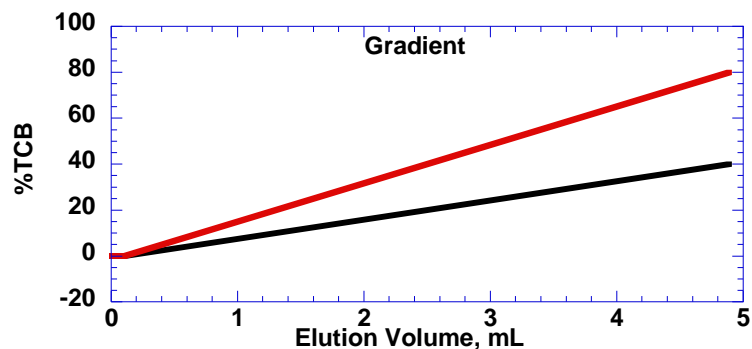
Two EP Copolymers by Different Gradients



Normalized Elution Curve



	Gradient %TCB/mL	wt% P average	wt%P (25%, high) - wt%P (25%, low)
EP1	8.35	87.4	5.6
EP2	16.7	86.8	11.5



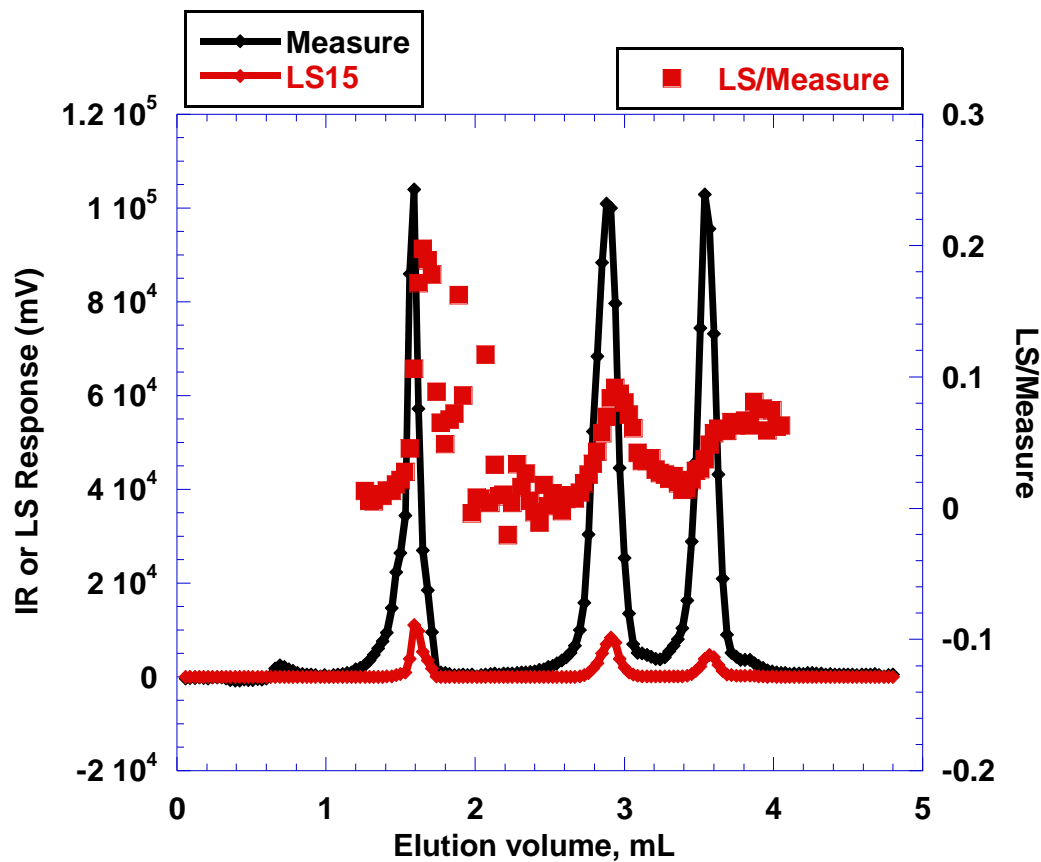
1. The metric (wt%P(25%,high)-wt%P(25%,low)) indicates the two samples have different chemical composition heterogeneities.

2. Same conclusion was drawn as that from the experiments using the same gradient (Slide 10). The metric is independent from the gradients.

Wt%P(25%, high) – Wt%P(25%, low) is an “absolute” metric for describing the breadth of the chemical composition distribution.

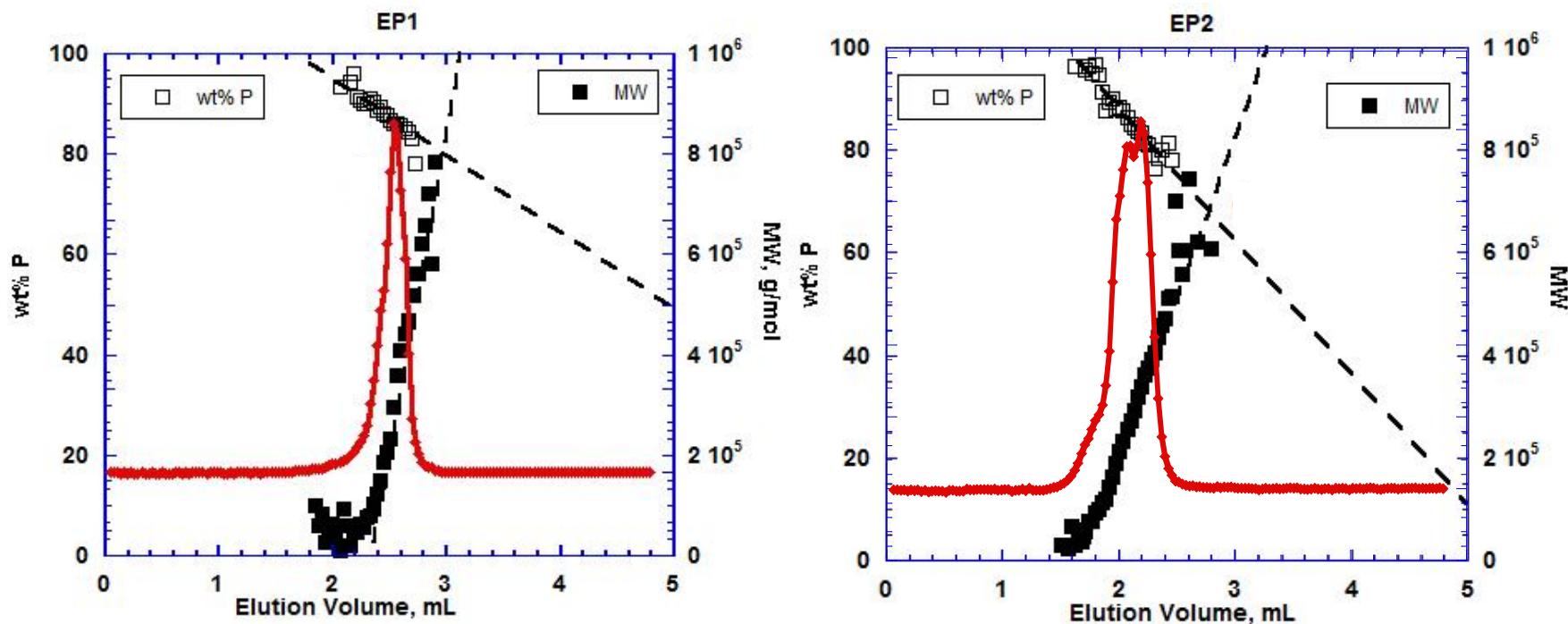
- 1. It is a metric that can be reproduced from lab-to-lab;**
- 2. It is a metric that can be used to understand the relationship between CCD and properties of polyolefins.**

Determine MW by LS



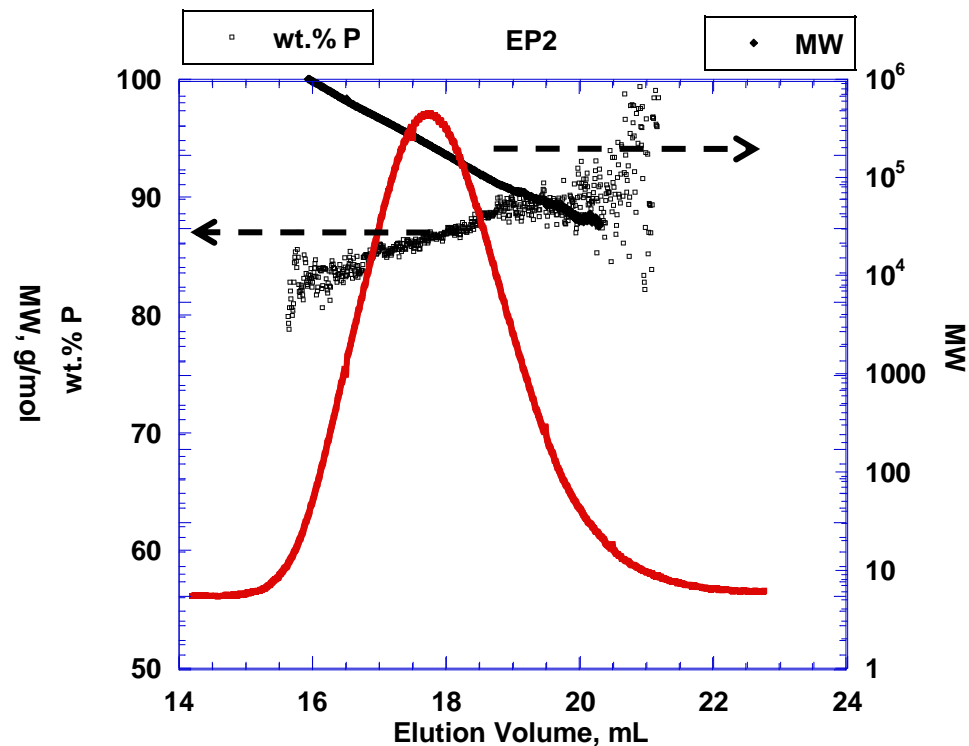
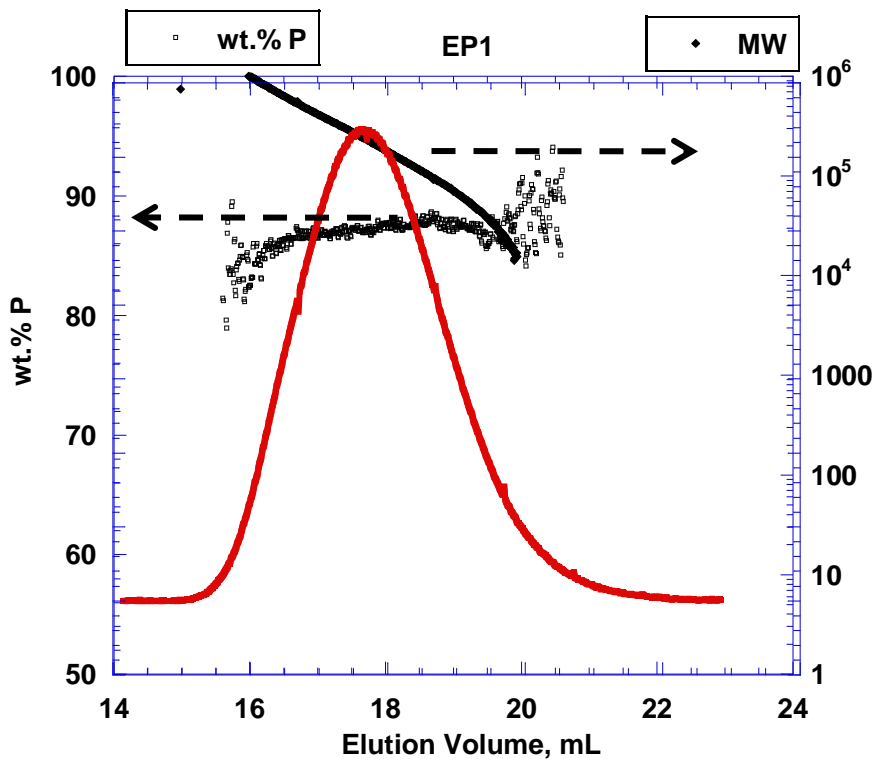
Mw of the separated fractions can be determined using light scattering detector (LS15).

Wt%P – Mw Correlation by HTLC X SEC



Both samples show negative correlations: high wt%P fractions have lower Mw.

LogMW-wt%P Correlation by SEC-LS/IR

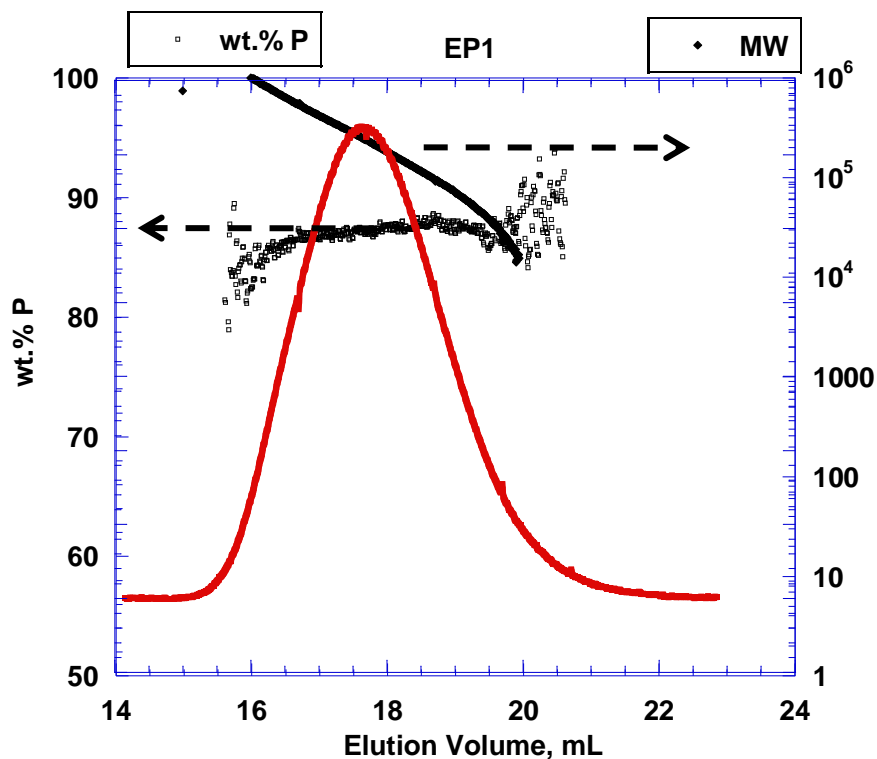


1. Both samples show high MW fractions have lower propylene contents.
2. EP2 shows higher increase of wt.% P as MW decreases.
3. Both item 1 and item 2 are consistent with the HTLC x SEC results.

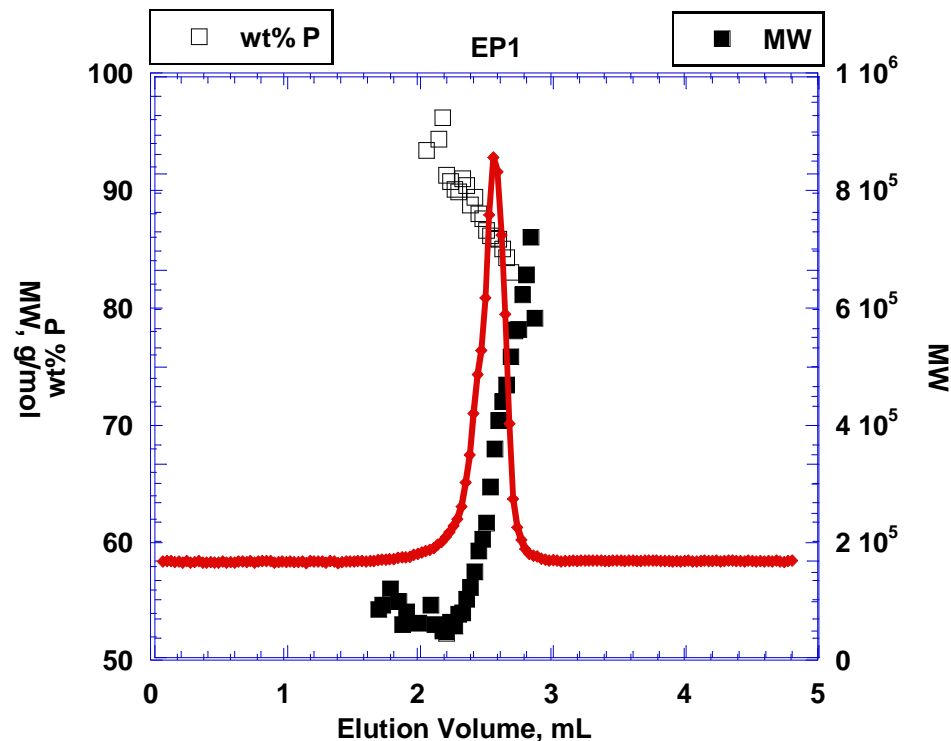
LogMW-wt%P vs Wt%P – Mw Correlations



SEC-LS/IR LogMW-wt%P



HPLC X SEC-LS/IR Wt%P-Mw



1. SEC sorts polymer chains by size (logMW). It cannot measure chemical composition heterogeneity.
2. Chemical composition – Mw correlation by HPLC x SEC is a more sensitive metric than logMW – chemical composition correlation by SEC.

- 1. SEC-LS/IR is not the method to measure chemical composition distribution.**
- 2. SEC-LS/IR measures the correlation between logMW and chemical composition.**
- 3. Chemical composition – Mw correlation by HTLC x SEC agrees with logMW – chemical composition correlation, but it is more sensitive because of high separation resolution.**

- 1. A technique was developed to measure chemical composition distribution of polyolefins in the range of 0 – 100% of ethylene, independent from crystallinity.**
- 2. An “absolute” metric was obtained for understanding the relationship between CCD and polyolefin properties.**
- 3. Mw of the fractions after chemical composition fractionation was determined, giving rise to the correlation between chemical composition and Mw.**

Acknowledgment



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