A Systematic Study on the Main Factors Affecting High-Temperature Thermal Gradient Interaction Chromatography (HT-TGIC)

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Acknowledgements

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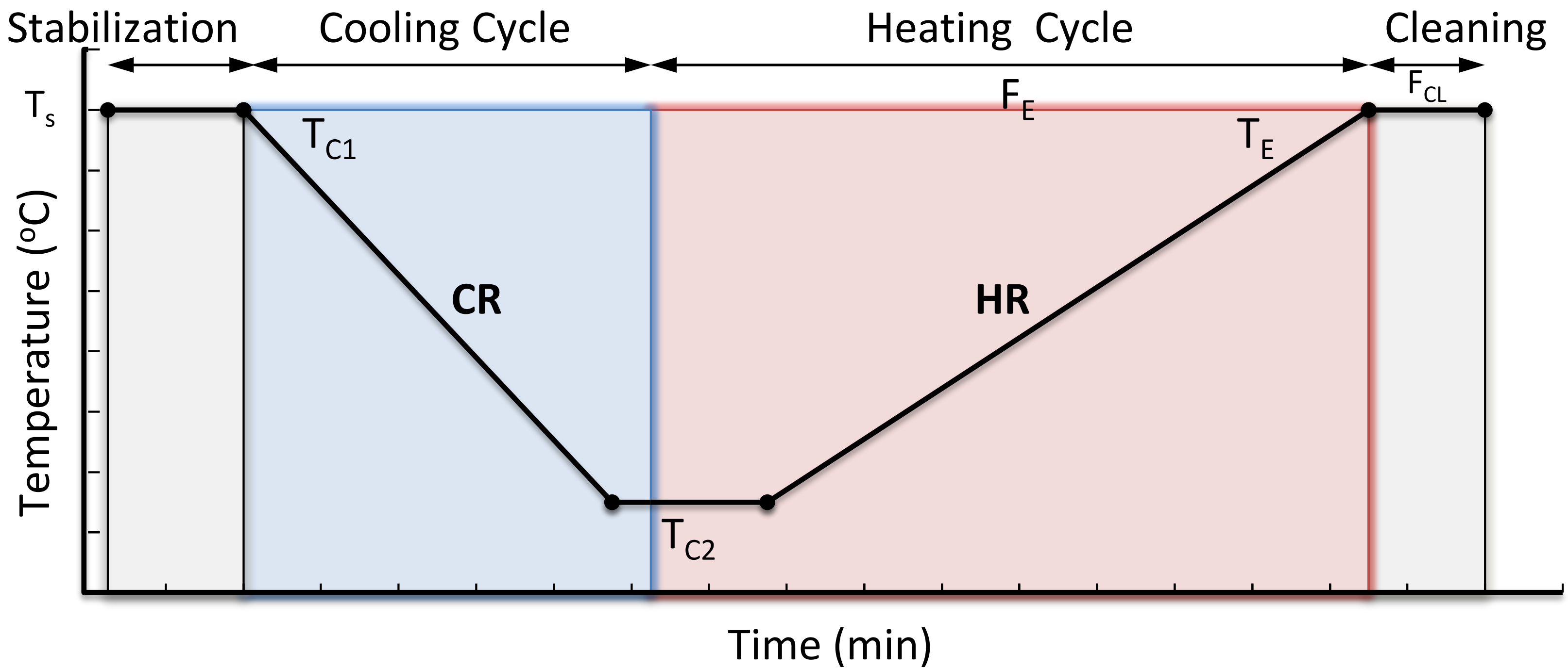
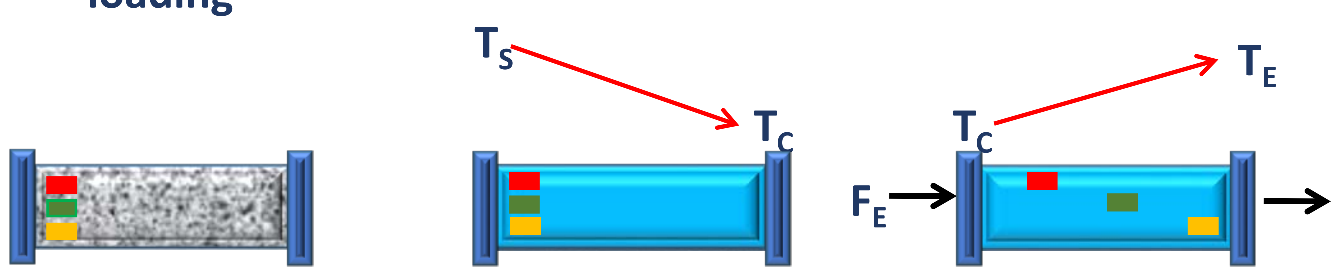
HT-TGIC Fractionation



Sample loading

Adsorption

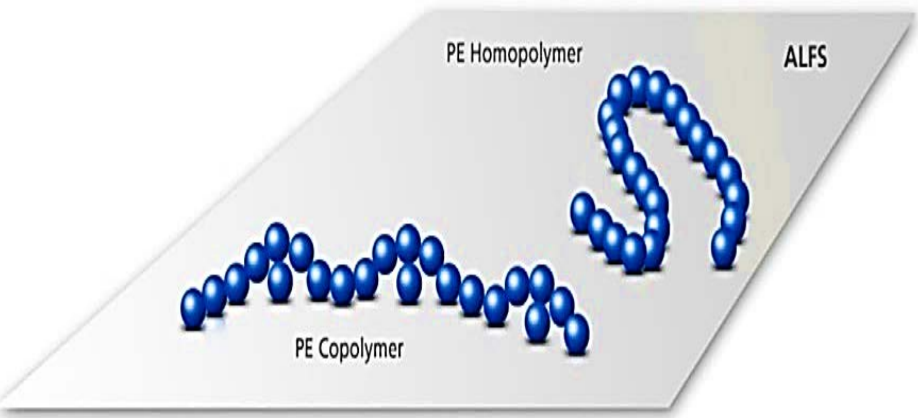
Desorption



HT-TGIC Fractionation Mechanism

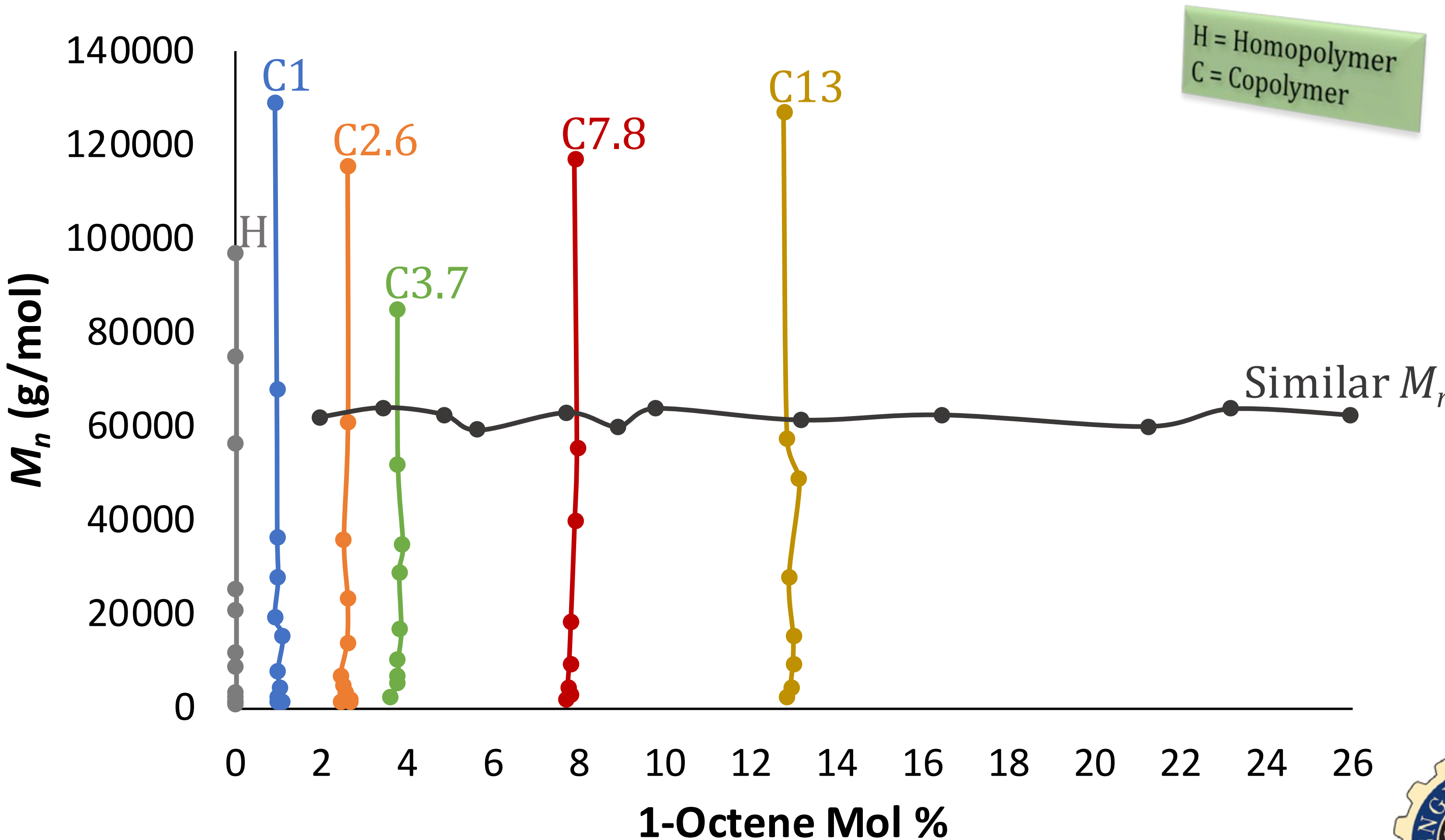
Hypotheses

- ❖ Adsorption strength depends on the available contact surface area between polymer chains and support.
- ❖ Atomic Level Flat Support (ALFS) surface.
- ❖ A sample with no or few SCBs interacts STRONGLY with the support.
  - ❖ Longer ES – Larger contact surface.
  - ❖ Adsorb at higher temperature.



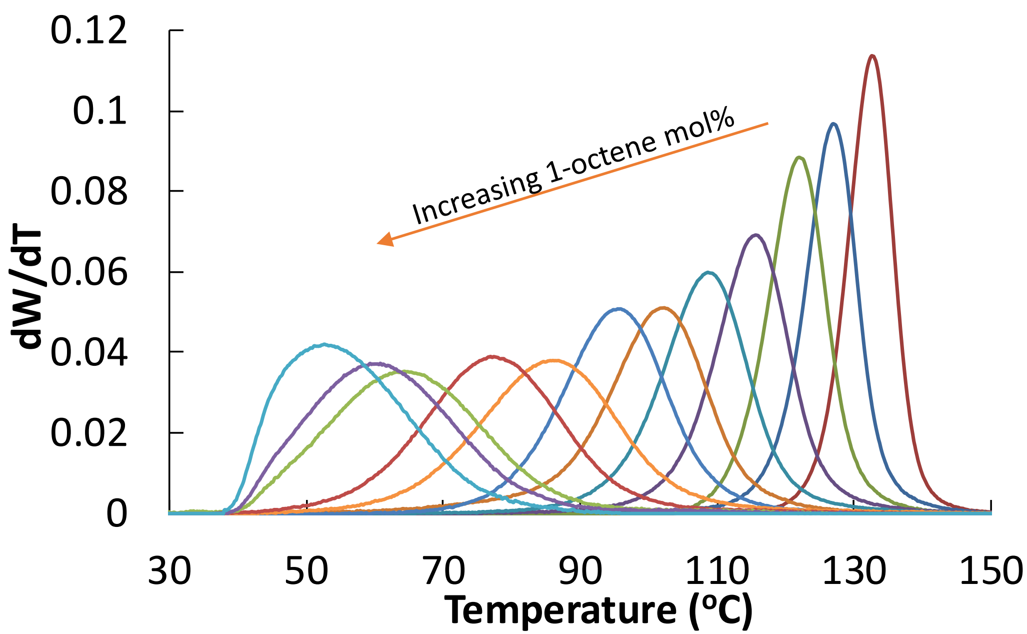
B. Monrabal, *Macromol. Symp.* **2015**, *356*, 147

Polyethylene Samples



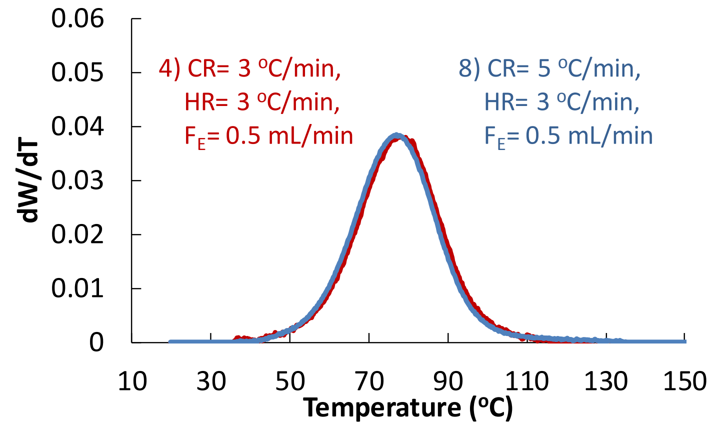
Comonomer Fraction Effect

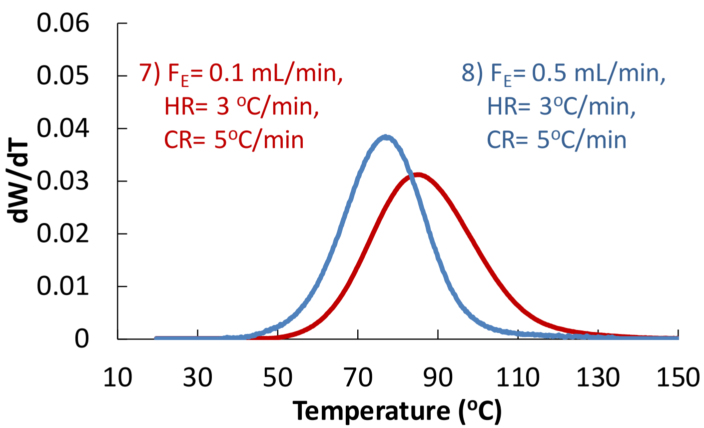
- Two main points were considered:
  - Elution peak temperature (T_P).
  - Standard deviation (σ).
- As 1-octene mol% increases HT-TGIC profiles become broader and shift to lower temperatures.
- SCBs formed by comonomer incorporation hinder chain adsorption and reduce T_P.

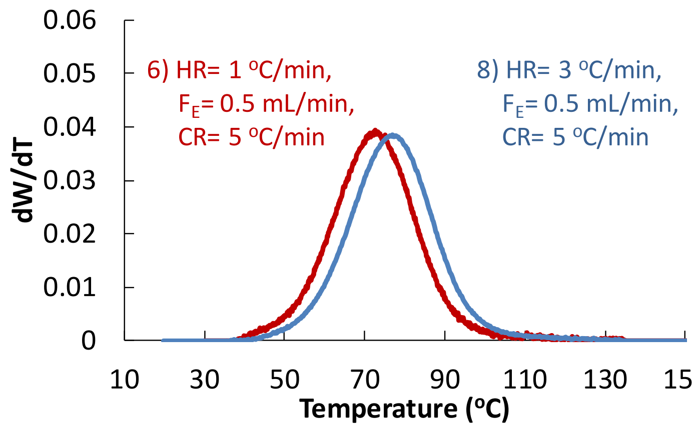


Influence of Operating Parameters: CR, HR, F_E

- **CR** has no significant effect of σ and T_P.
- **HR** & F_E as well as their interactions affect both σ and T_P.

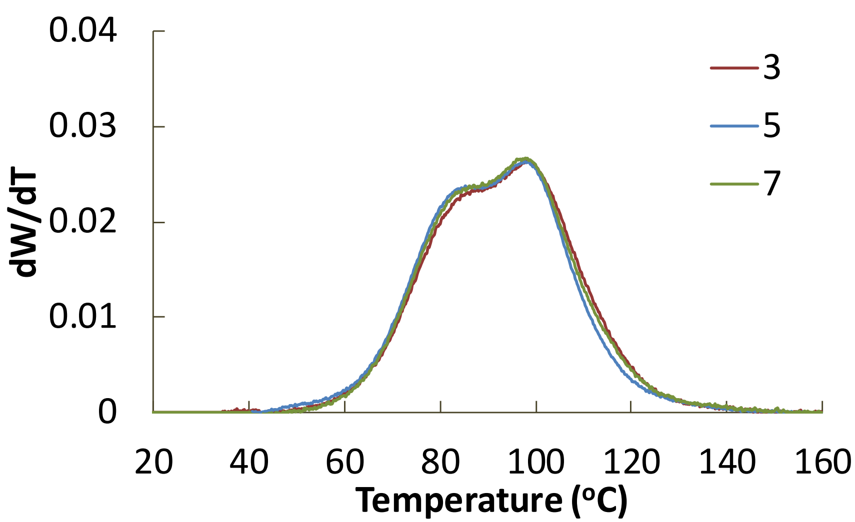


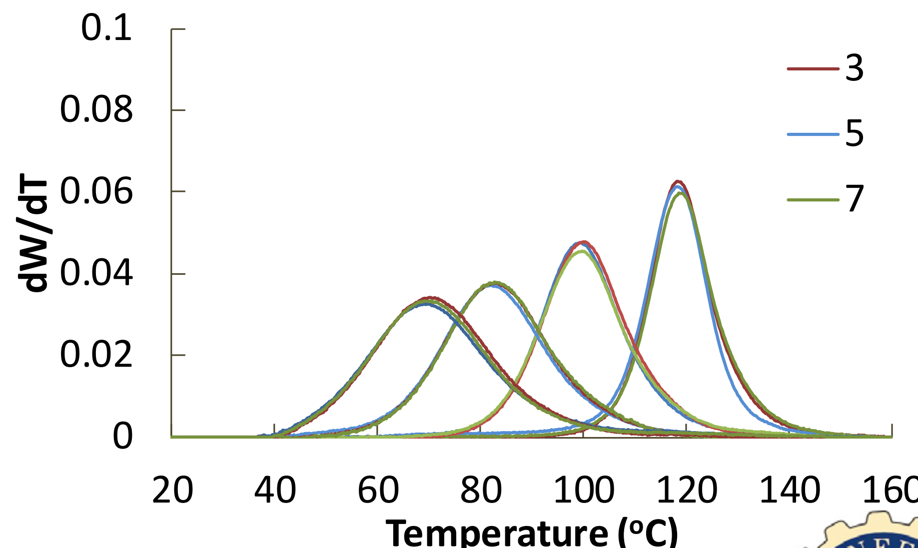




Influence of Packing Particle Size

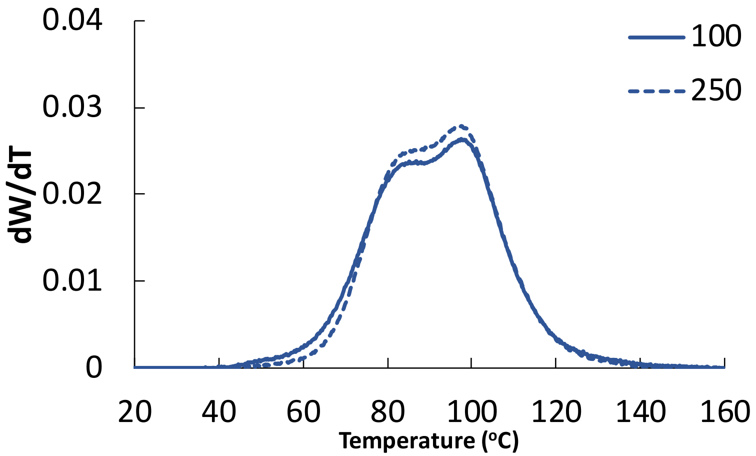
- Three particle sizes (3, 5, and 7 μm), same column length (100 mm).
- Particle size has NO significant effect on σ and T_P of individual samples and binary blends.

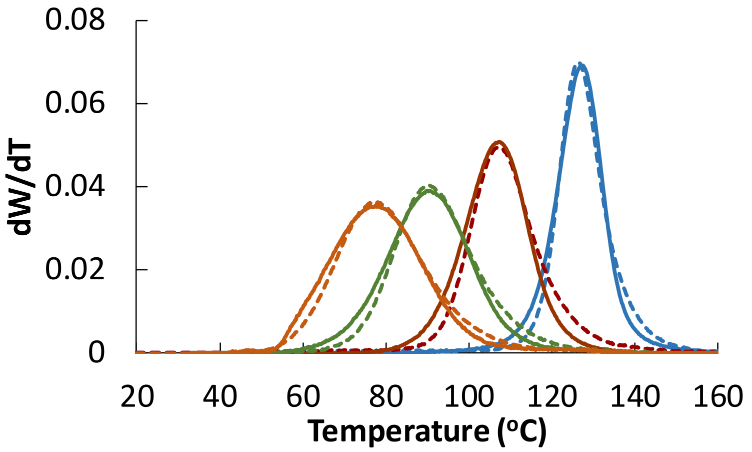




Influence of Column Length

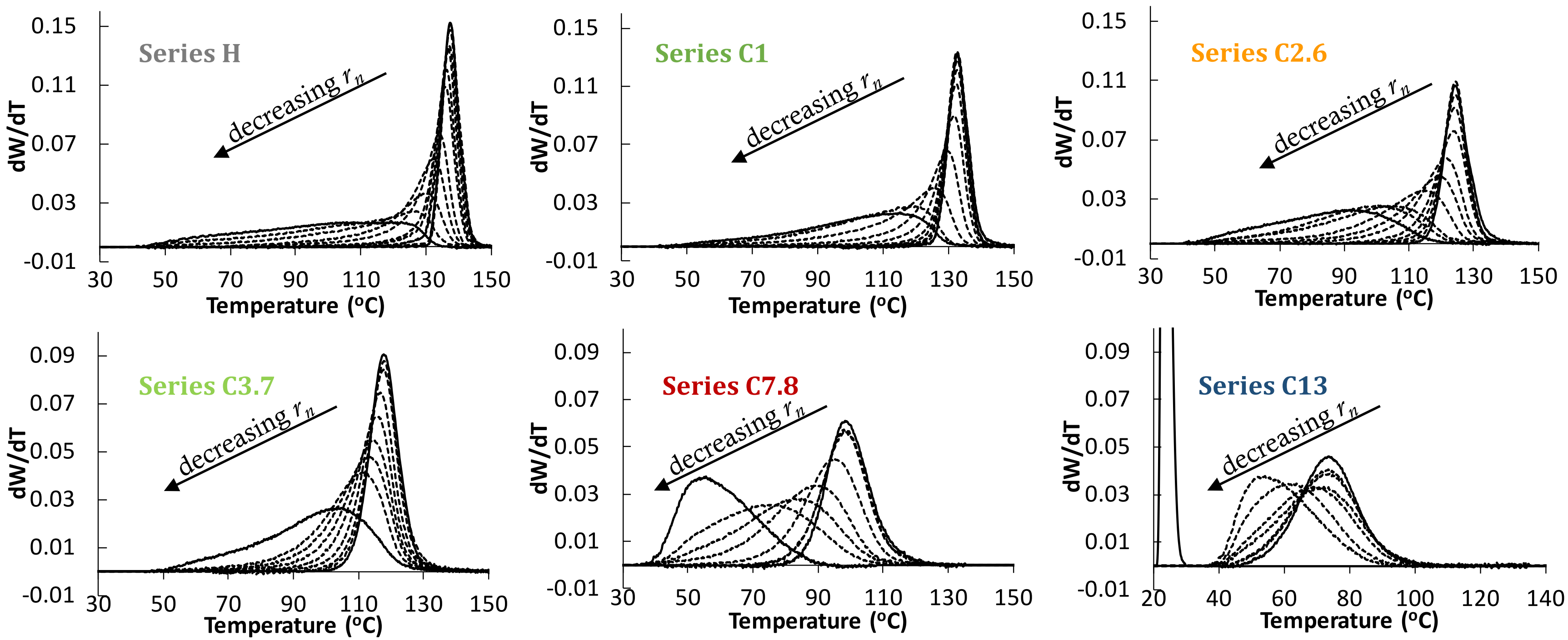
- Two column lengths (100, 250 mm), same particle size (5μm).
- Column length has a small effect of σ, but shifted T_P to higher values.



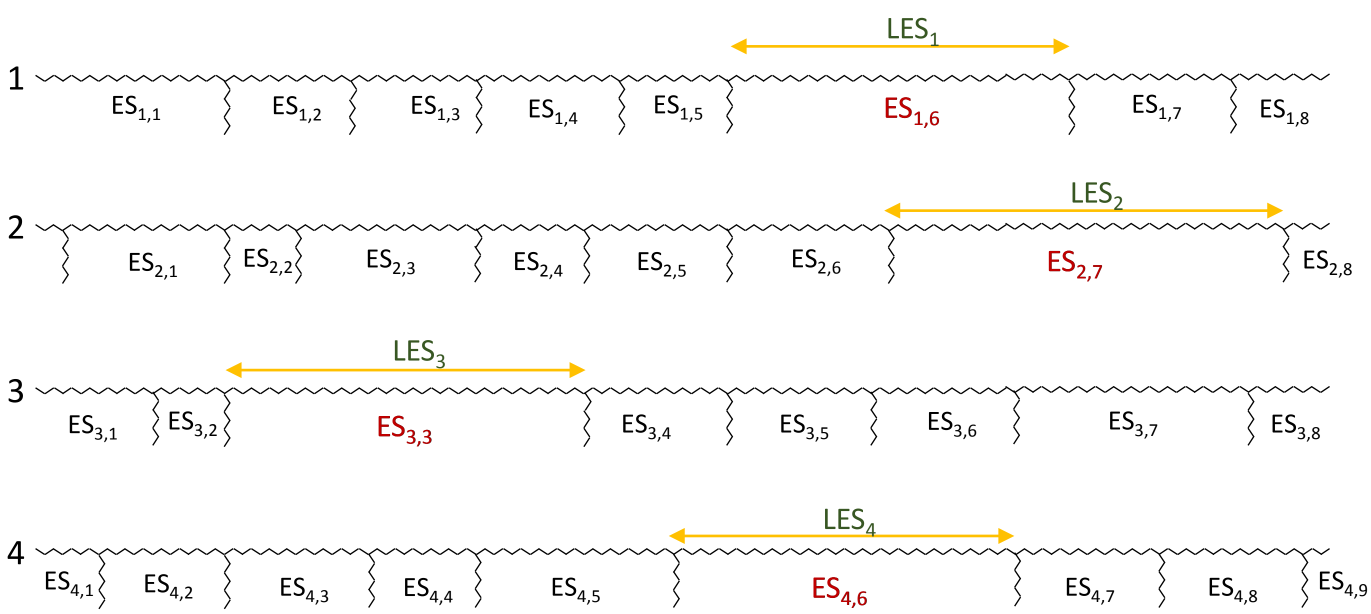


Chain Length and 1-Octene Mole Fraction

- HT-TGIC profiles broaden and shift to lower temperatures when r_n decreases.



AES Average Ethylene Sequence Length
LES Longest Ethylene Sequence Length

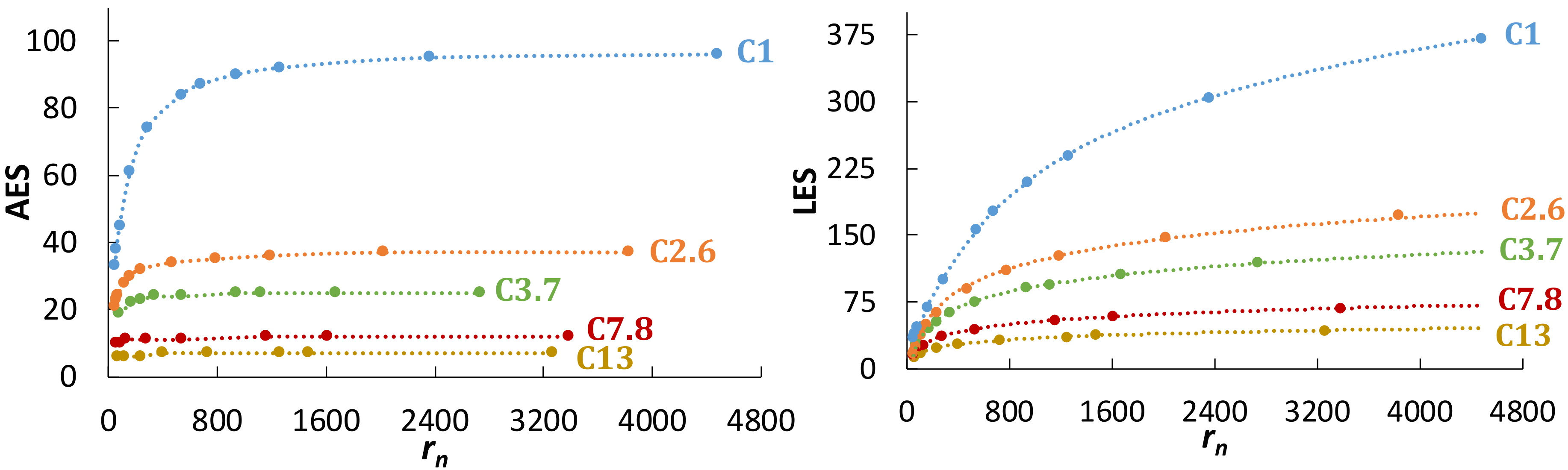


$$AES = \frac{\sum_i \sum_j ES_{i,j}}{n}$$

$$LES = \frac{ES_{1,6} + ES_{2,7} + ES_{3,3} + ES_{4,6}}{4}$$

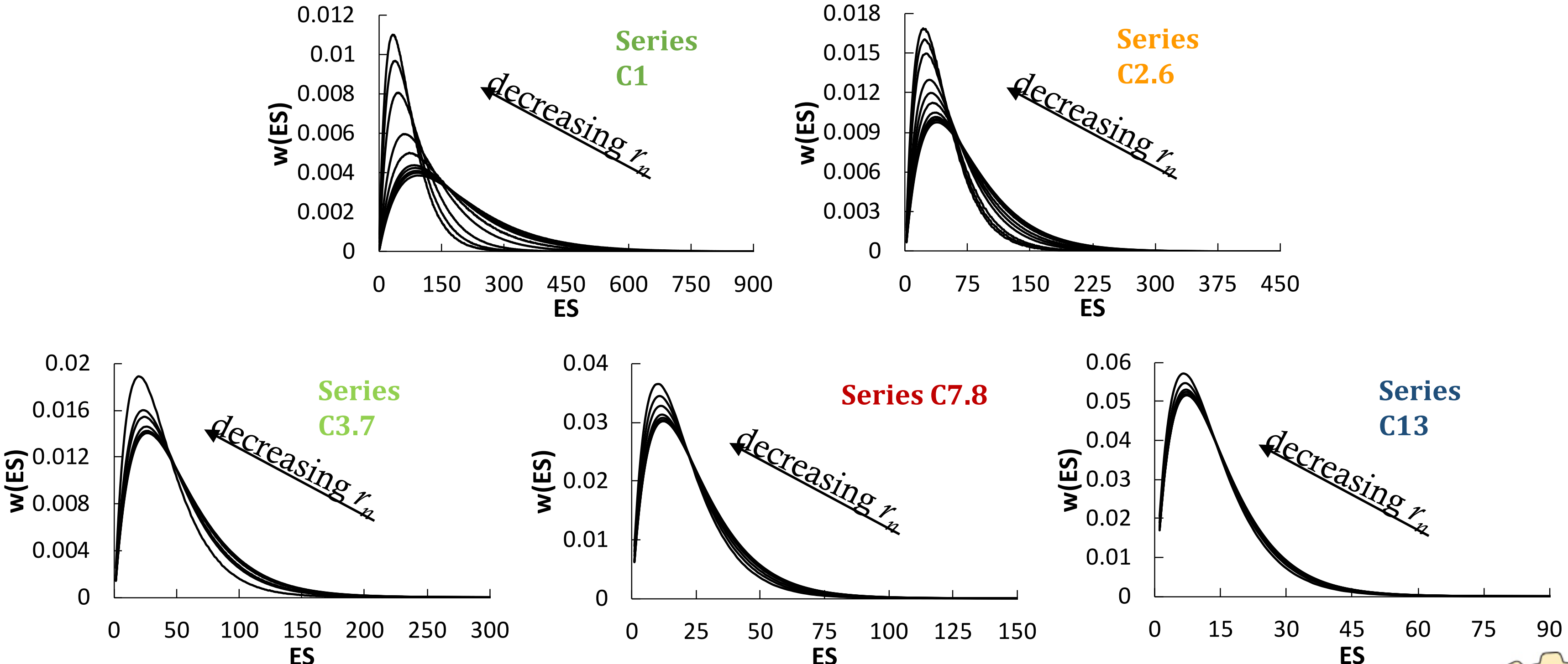
r_n x AES and r_n x LES

- AES depends only **WEAKLY** on r_n, especially for copolymers with higher comonomer fractions.
- LES depends more strongly on r_n, but less so for copolymers with higher comonomer fractions.



w(ES)
Distribution of AVERAGE Ethylene Sequences

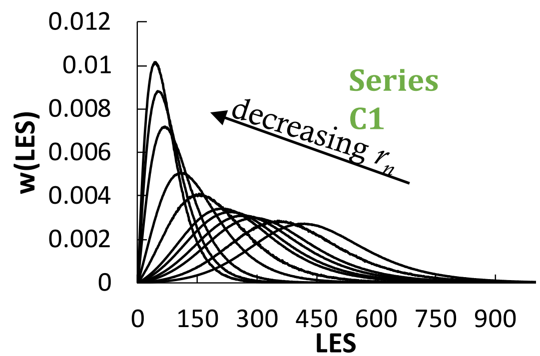
❖ w(ES) does **NOT** depend on copolymer molecular weight, particularly for samples with higher 1-octene fraction.

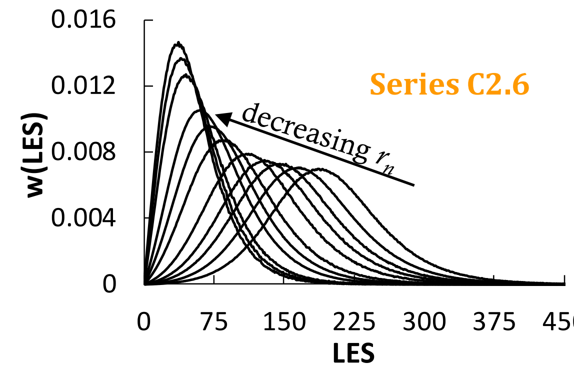


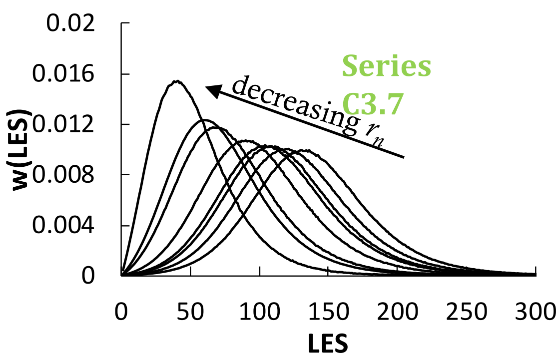
w(LES)
Distribution of LONGEST Ethylene Sequences

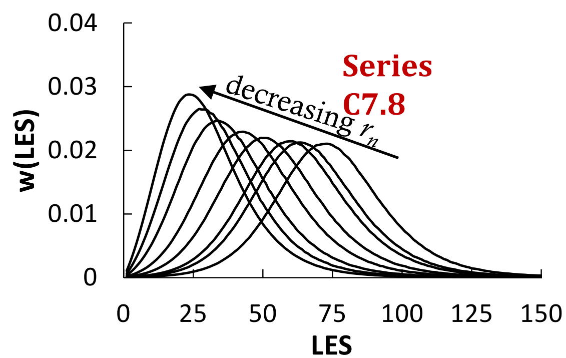
- W(LES) shifts to lower averages and becomes narrower, **NOT** broader when r_n decreases.

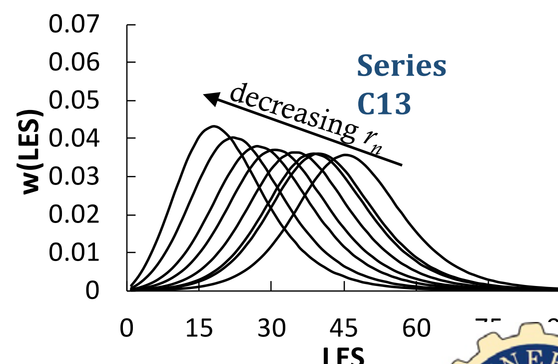
- w(ES) and w(LES) cannot explain the shapes of experimental HT-TGIC profiles.





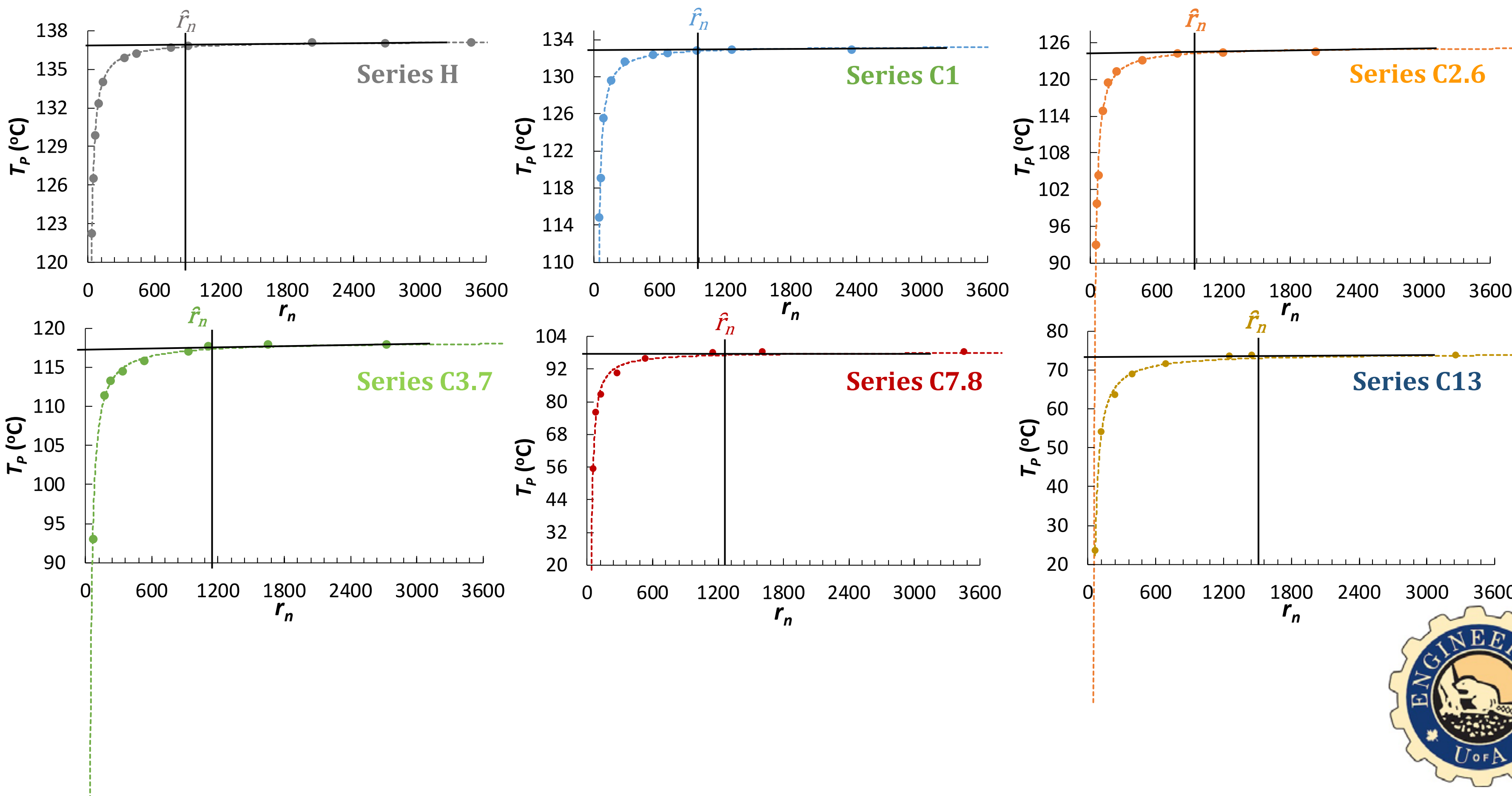






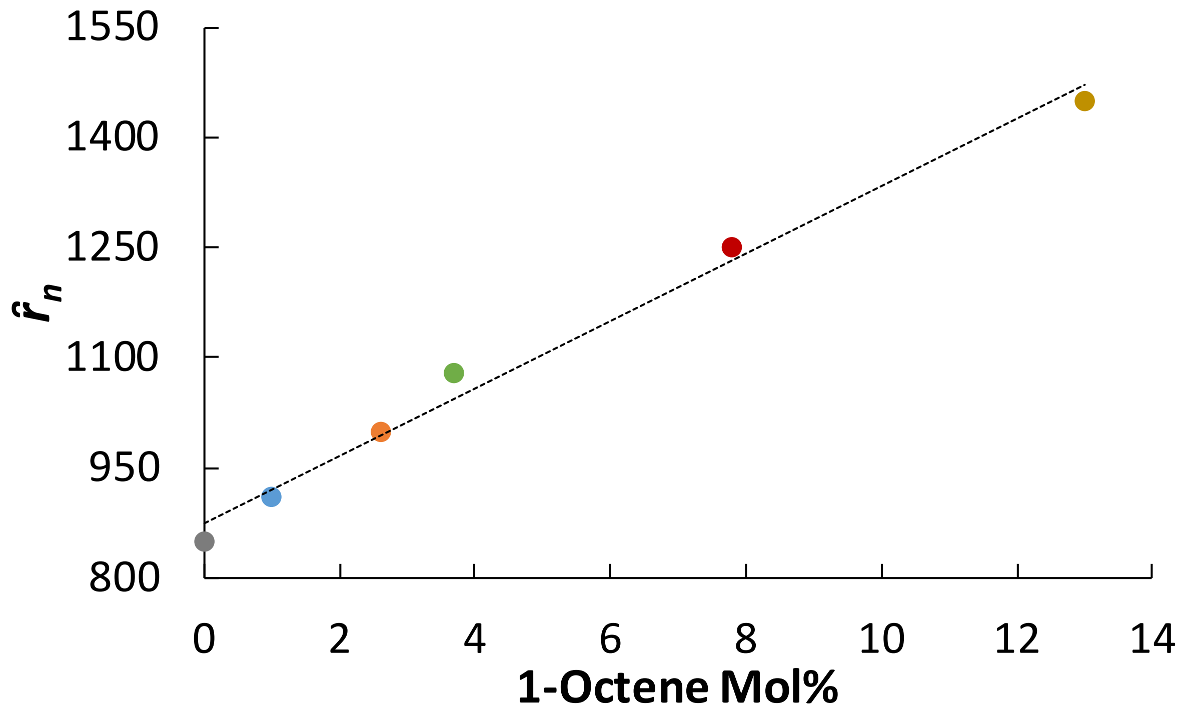
T_p x r_n

- T_P decreases exponentially below a critical value of r_n ($\hat{r}_n$).



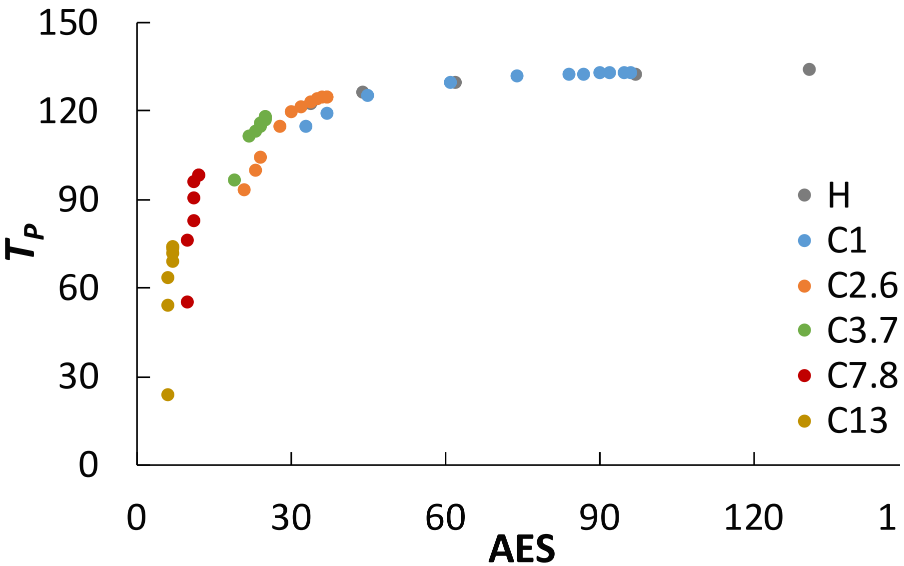
Critical r_n - $\hat{r}$

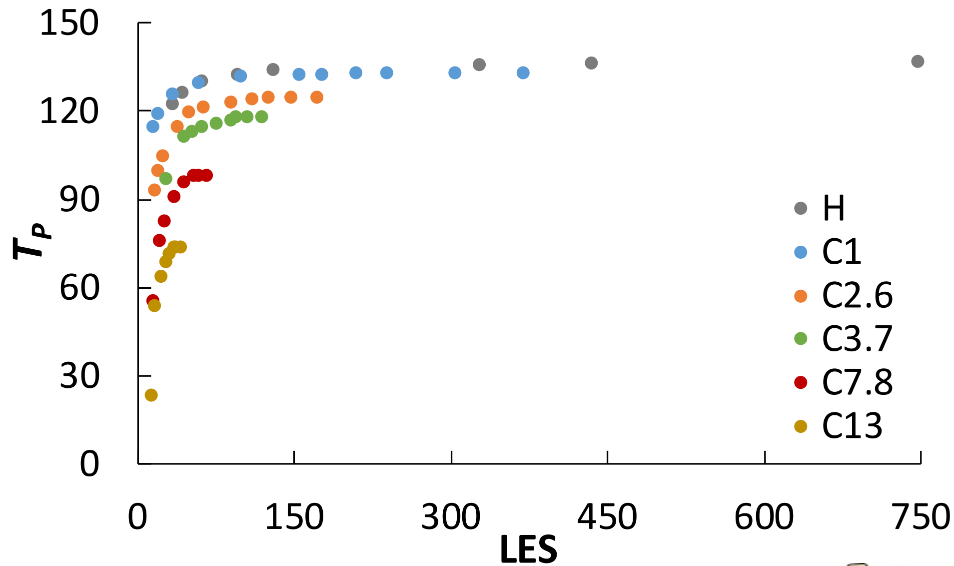
- The critical r_n ($\hat{r}_n$) increases linearly with increasing of 1-octene fraction in the copolymer.
- $\boldsymbol{r_n}$ effect is more pronounced for copolymers with increasing 1-octene fraction.



T_p versus AES and LES

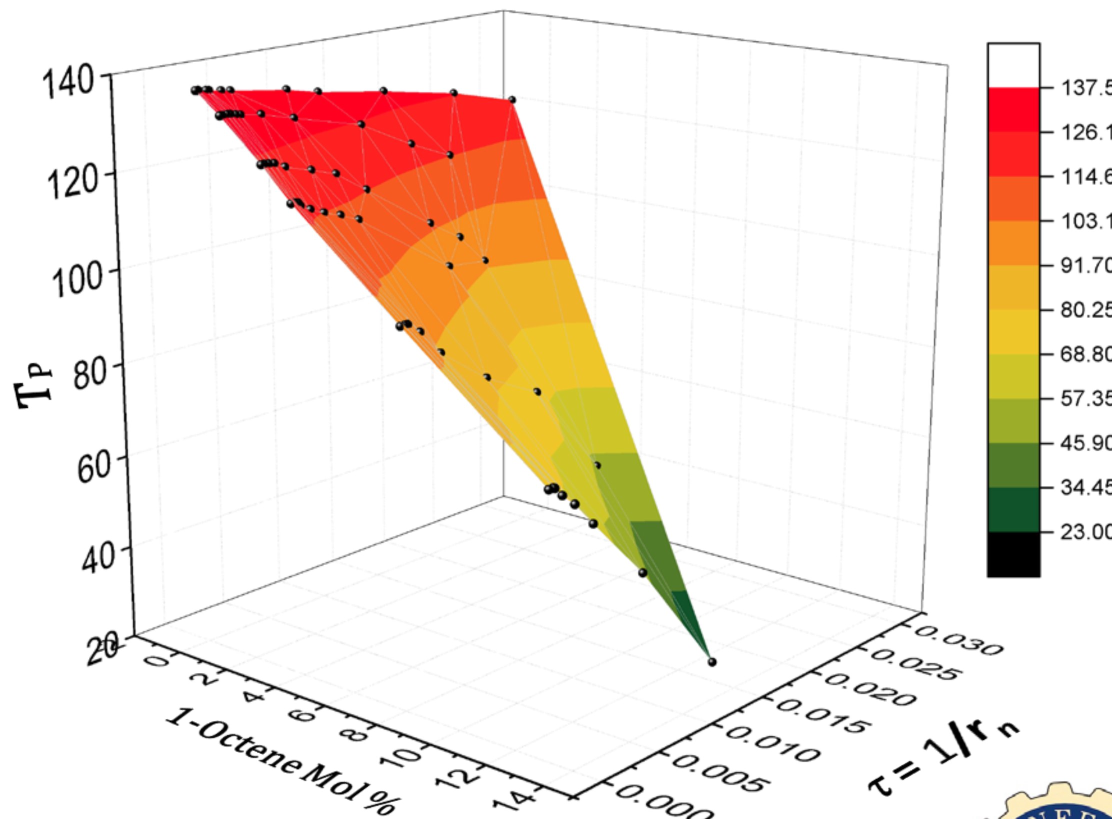
- Copolymers with different AES or LES have the same T_p .
- Neither AES nor LES explain the shift in HT-TGIC peak temperature below $\hat{r}_n$.





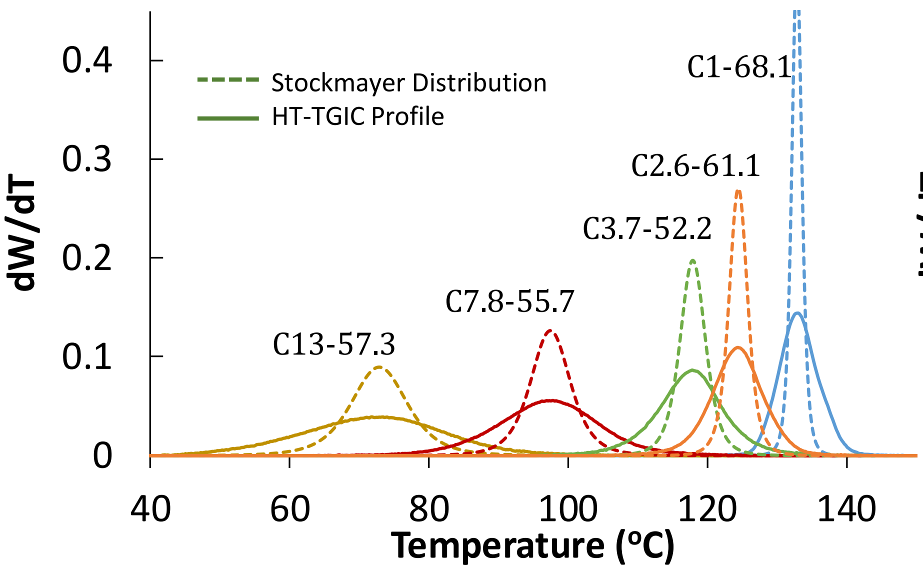
Joint Effect of Chain Length and 1-Octene Mole Fraction on T_p

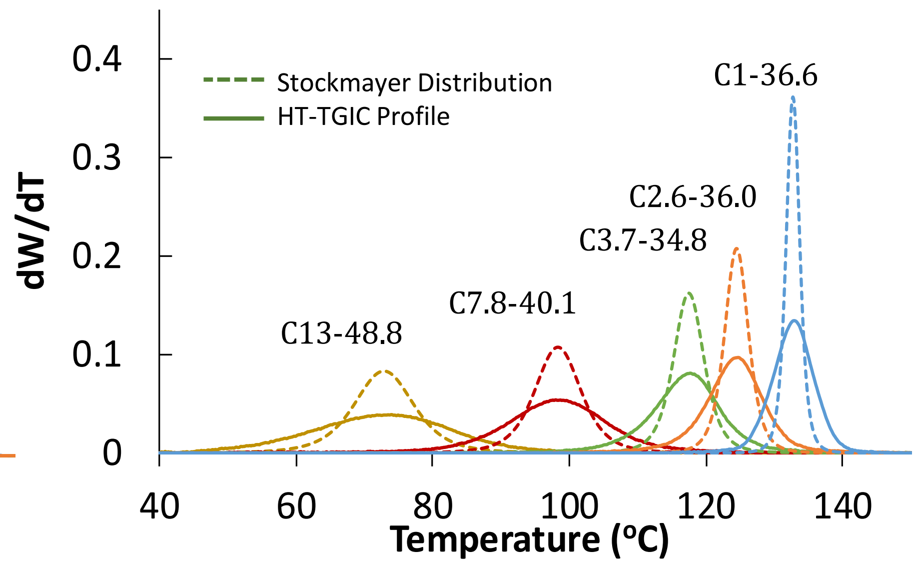
- Linear relation between T_P and τ for samples below the critical value of r_n.
- HT-TGIC profiles are more sensitive to chain length effect for higher 1-octene fraction series.



Using Stockmayer Distribution to Describe HT-TGIC Profiles Above the Critical r_n

- HT-TGIC profiles are broader than predicted by Stockmayer distribution.
- Is axial dispersion responsible for these differences?





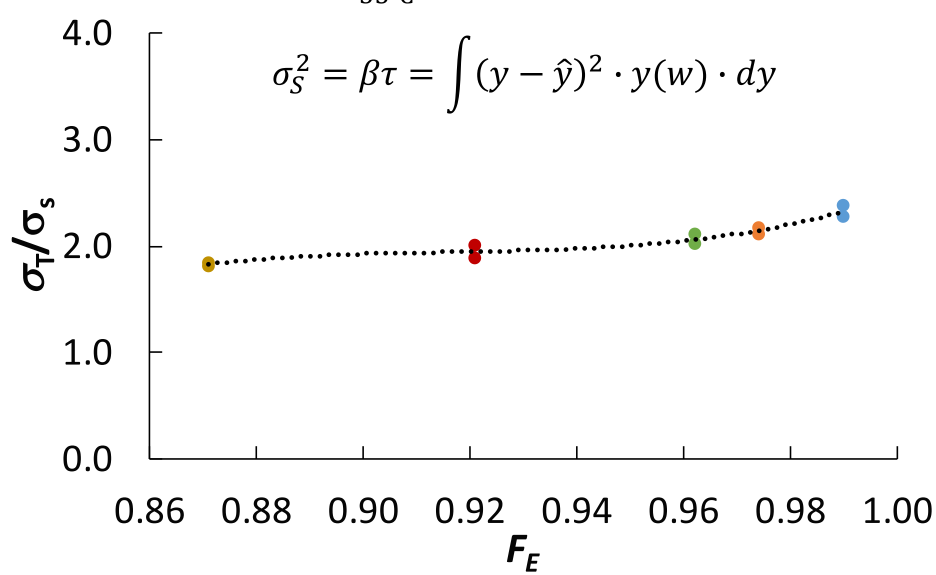
Axial Dispersion Correction - σ_T/σ_S

- The σ_T/σ_S ratio is nearly constant for all samples, increasing only slightly for samples with higher ethylene fraction.

- *Hypothesis*: Axial dispersion in HT-TGIC is ***independent*** of the 1-octene fraction for these samples.

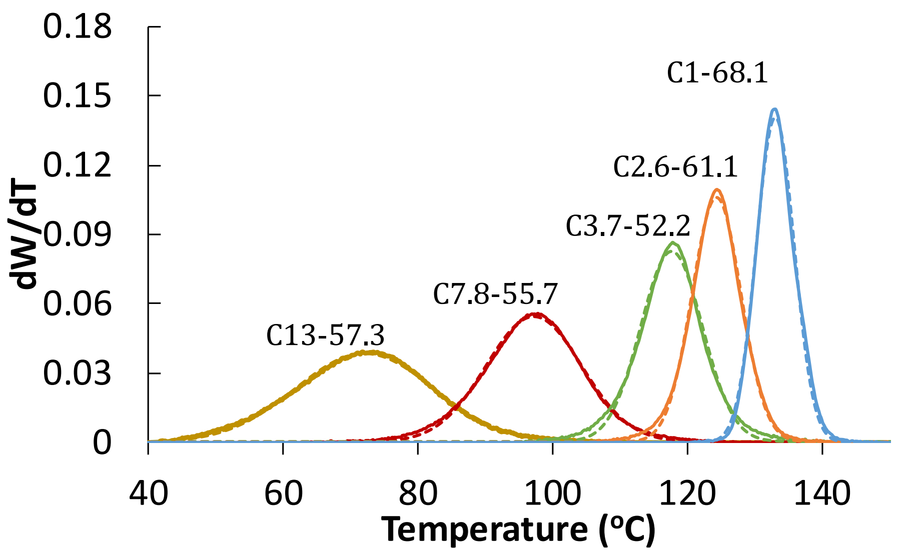
$$\sigma_T^2 = \int_{35°C}^{160°C} (T - T_\mu)^2 \cdot f(T) \cdot dT$$

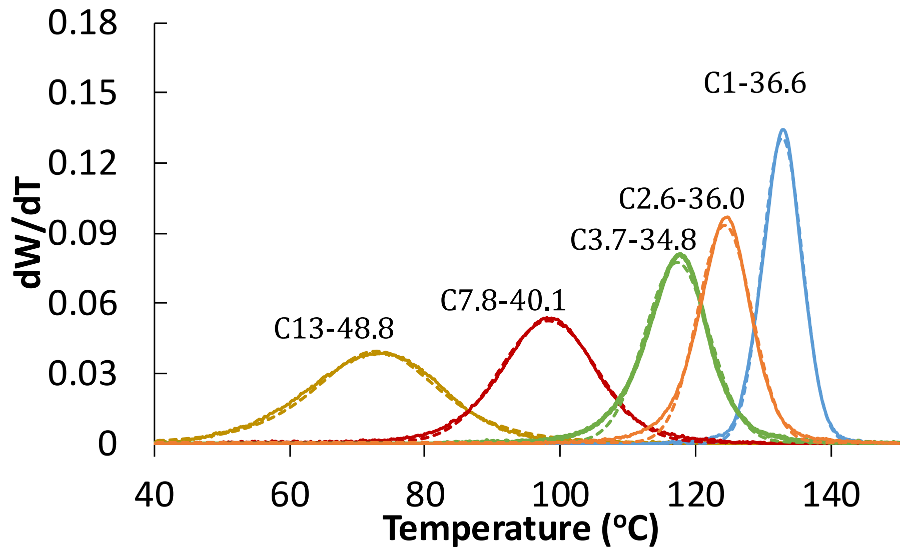
$$\sigma_S^2 = \beta\tau = \int (y - \hat{y})^2 \cdot y(w) \cdot dy$$



Adjusted Stockmayer Distributions

- Stockmayer distributions were adjusted by substituting $\beta\tau\ (\sigma_S^2)$ by (σ_T^2).
- The "broadened" Stockmayer distribution *fits* well all HT-TGIC profiles.

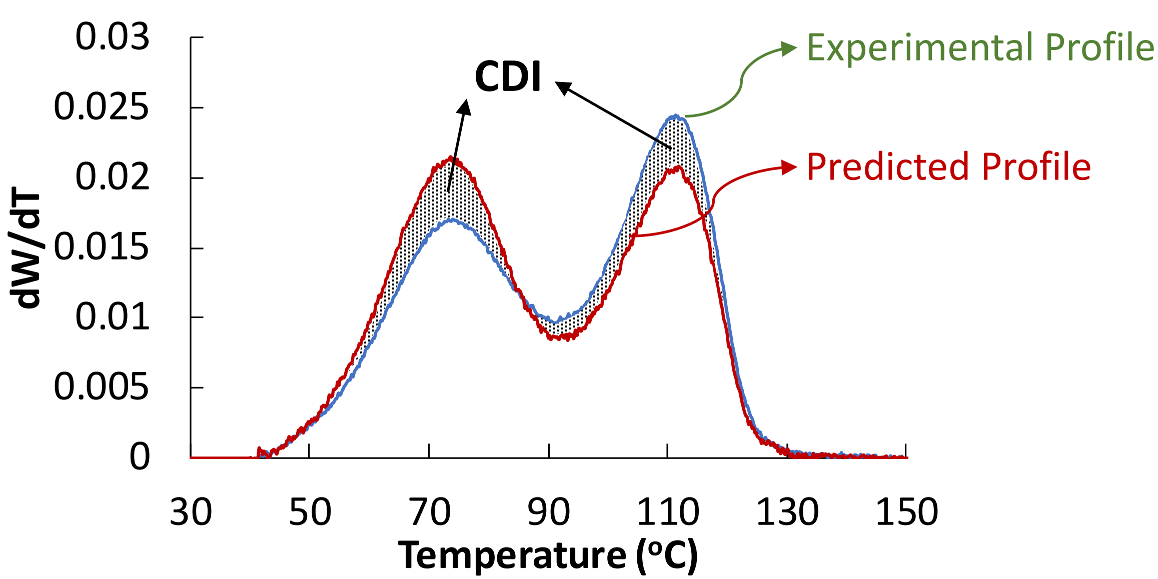




Binary Blend Investigations

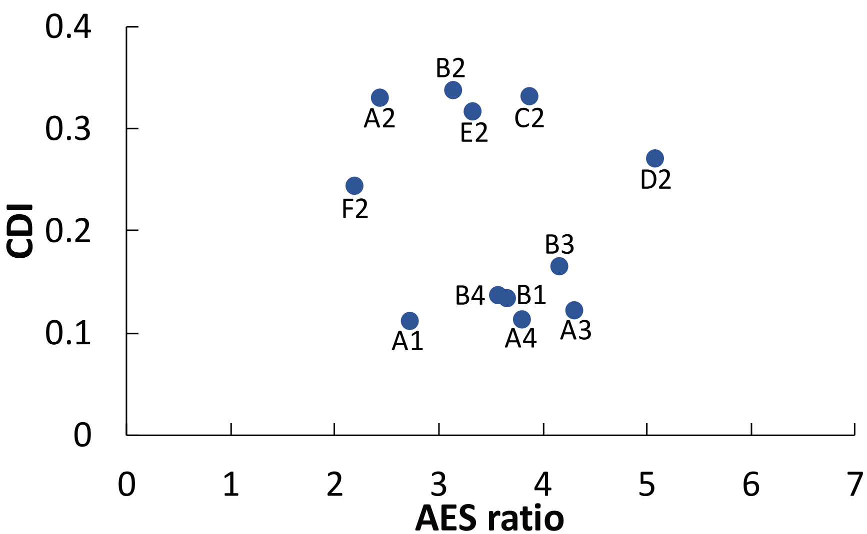
Blend Samples - Group A and Group B

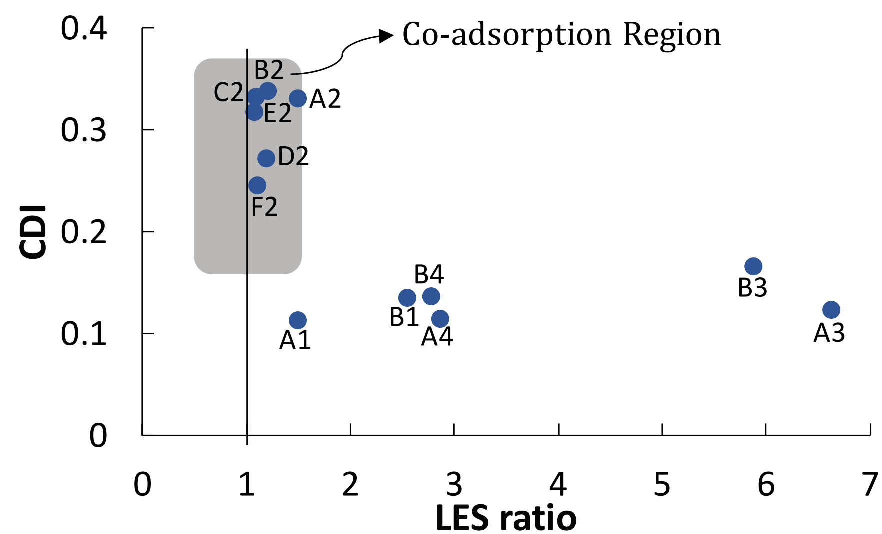
- Two blend groups (A & B) were chosen to study the effect of $\boldsymbol{r_n}$ and mole fraction of 1-octene on HT-TGIC fractionation
- **CDI** quantifies co-desorption



Trying to Understand CDI with AES and LES

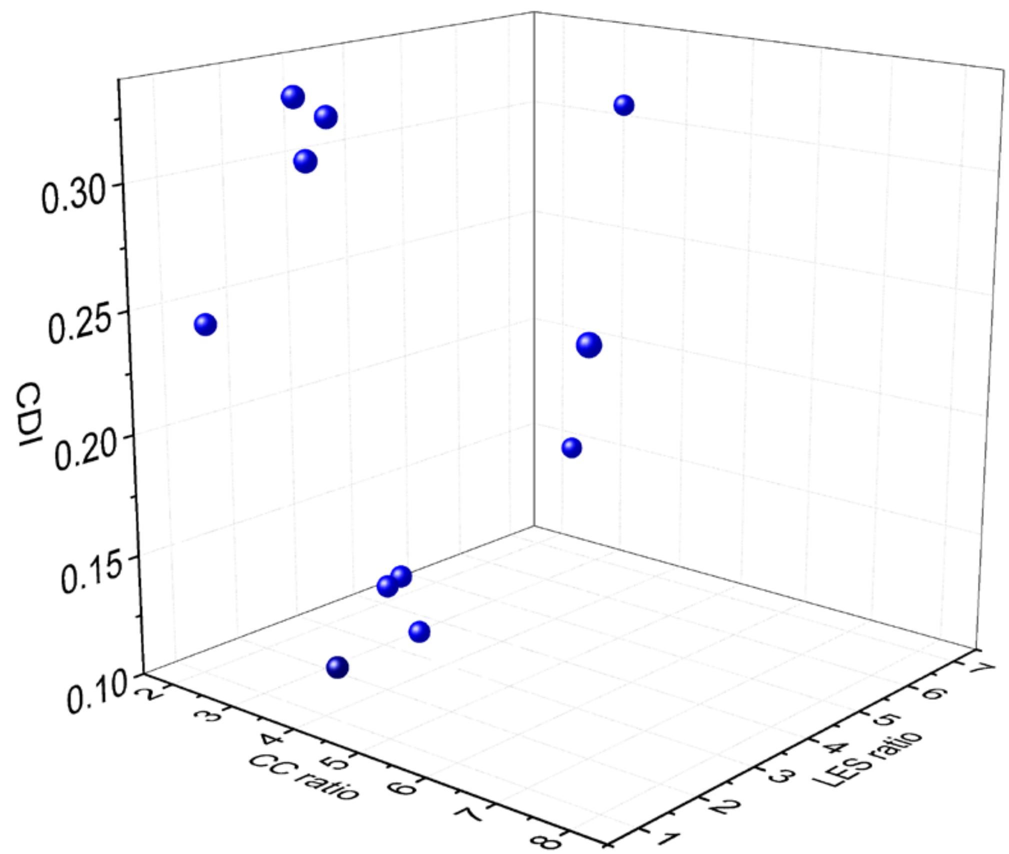
- CDI does **NOT** correlate with the AES ratio of the blend components.
- Most samples having LES ratios close to 1 have a relative high CDI.





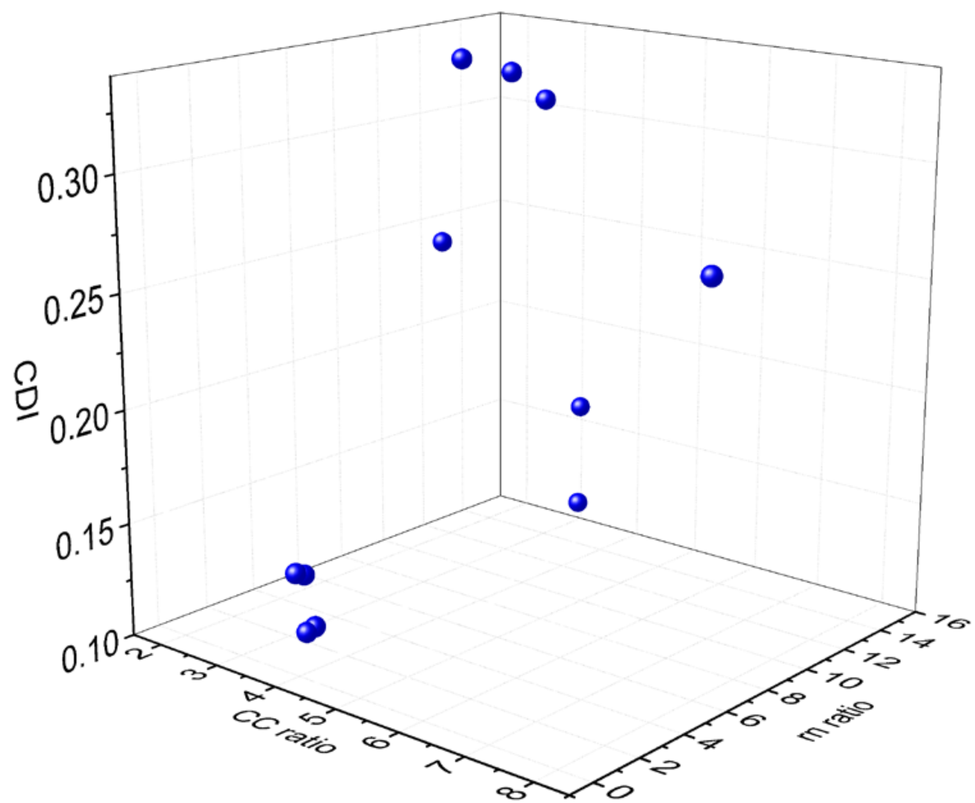
CDI x CC ratio and LES ratio

- The effect of chemical composition (CC) ratio can not b ignored.
- For a given CC ratio, CDI increases when the LES ratio increases.
- For the same LES ratio, CDI increases the CC ratio decreases
- Similar CC, not similar LES, correlate with CDI on HT-TGIC supports.



CDI x CC ratio and r_n ratio

- For a given CC ratio, chains with more dissimilar $\boldsymbol{r_n}$ will have a higher CDI.
- For a given $\boldsymbol{r_n}$ ratio, CDI increases when the CC ratio decreases.
- Similar CC, not similar r_n, correlated with CDI on HT-TGIC supports.



Conclusions

❖ Influence of analytical operation conditions:

- CR had no significant influence on the values of $\boldsymbol{T_P}$ or the shape of HT-TGIC profiles.
- HR and F_E and their interactions affect HT-TGIC peak temperature and breadth.
- The preferred analytical conditions (CR= 5 °C/min, HR= 3 °C/min, F_E=0.5 ml/min) can reduce the co-desorption index and minimize the analysis time.

❖ Effect of Hypercarb column:

- Neither average particle size nor column length played an important role to enhance the resolution of HT-TGIC profile of polyolefins and their blends.
- It is preferable to use shorter columns with larger particles.

Conclusions

❖ Joint effect of chain length and 1-octene mole fraction:

- In each series, the T_P of each polymer series decreased exponentially below $\hat{r}_n$, and the profile broadens.
- LES and AES distributions did not provide an adequate correlation between the shape and peak position of HT-TGIC profiles and ethylene sequences.
- Stockmayer distribution describes the shapes of HT-TGIC profiles correctly, but systematically predicts narrower distributions than the experimental ones.
- Axial dispersion may cause the observed peak broadening in HT-TGIC profiles
- Similar LESs of blend components do not explain co-desorption.

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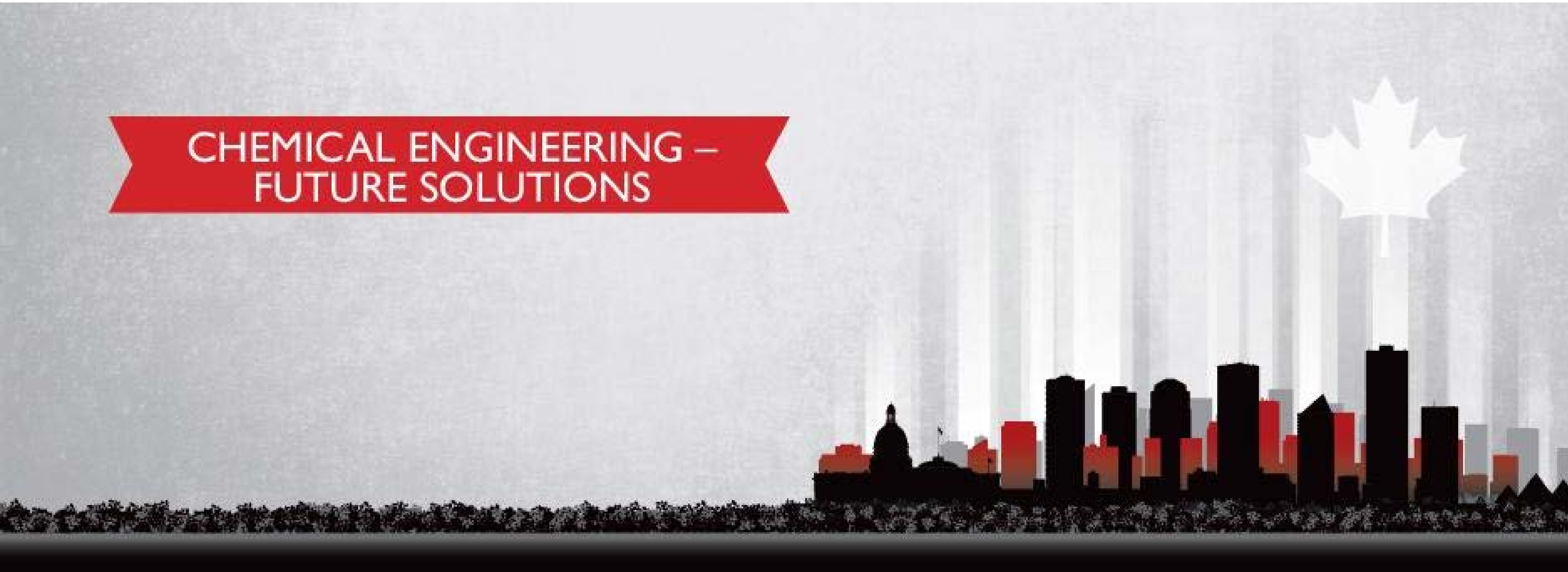

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