Uncertainty analysis of Inferring CCD using Crystaf

Arsia Takeh, Sachin Shanbhag

Department of Scientific Computing, Florida State University, Tallahassee, FL

CCD of Random Copolymers

Physical properties of copolymers are influenced by how comonomer units are distributed on the copolymer chains. One of the important distributions that is used to describe them is chemical composition distribution (CCD), it describes the distribution of the average comonomer content of the copolymer chains, thus reflecting intermolecular heterogeneity. The relationship between the CCD of copolymers and their mechanical and thermal properties is one of the important structure-property relationships that have to be properly quantified for polyolefins. In order to establish these structure-property relationships, one needs to have an analytical technique that can accurately determine the CCD of copolymers.

In the case of semi-crystalline copolymers, we used crystallization analysis fractionation (Crystaf)[1]. Crystaf fractionate polymer chains according to their crystallizabilities via crystallization from dilute solution.
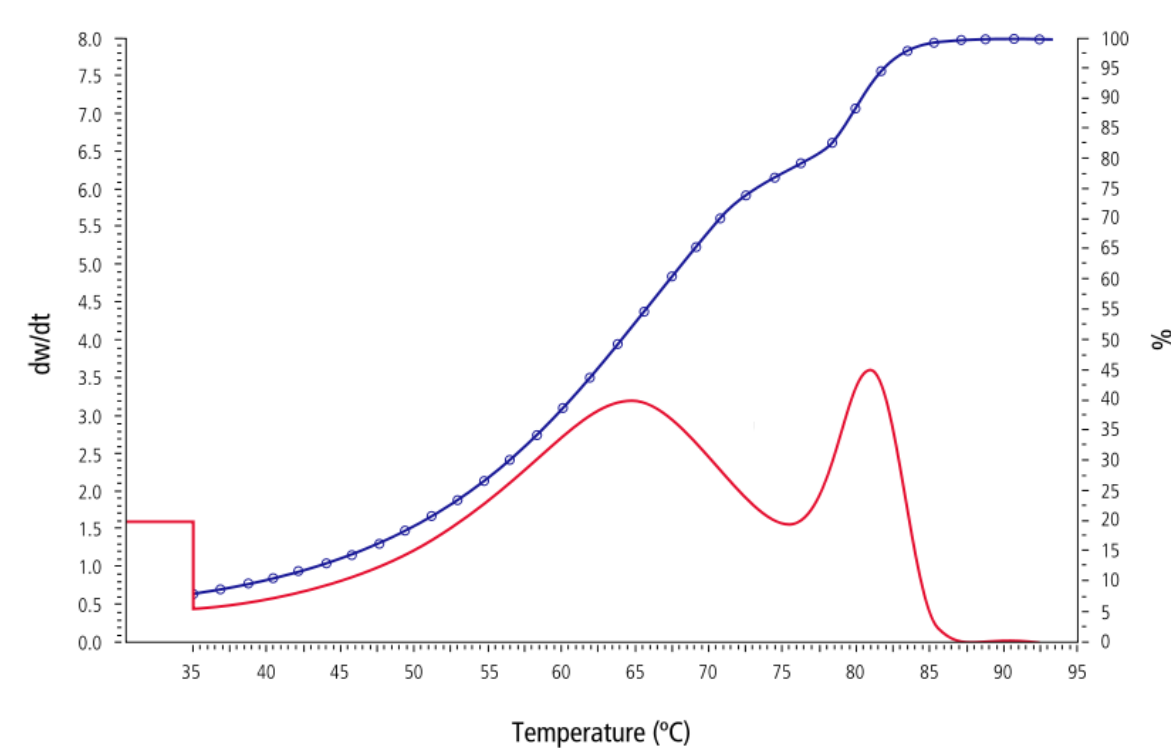

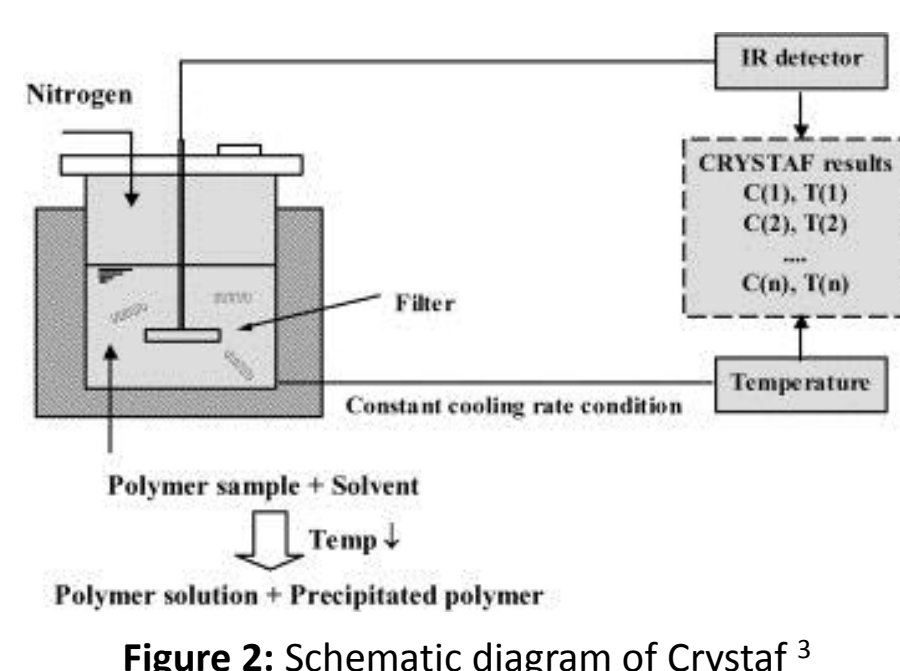**Figure 1:** Cumulative and differential Crystaf of an LLDPE resin [2]

Figure 2: Schematic diagram of Crystaf [3]

Mathematical Modelling of Crystaf for Copolymers

In ethylene--olefine copolymers the LES (longest ethylene sequence) is considered to be the key factor.
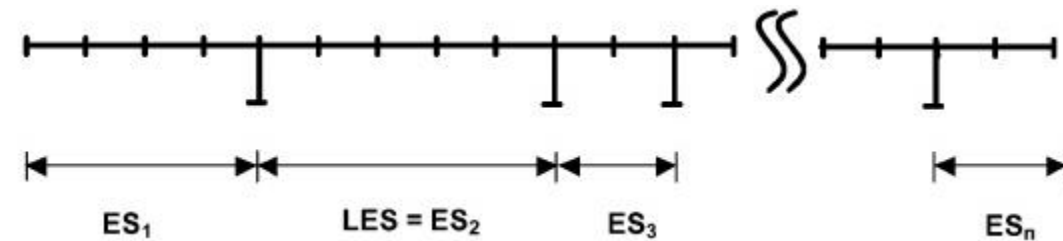

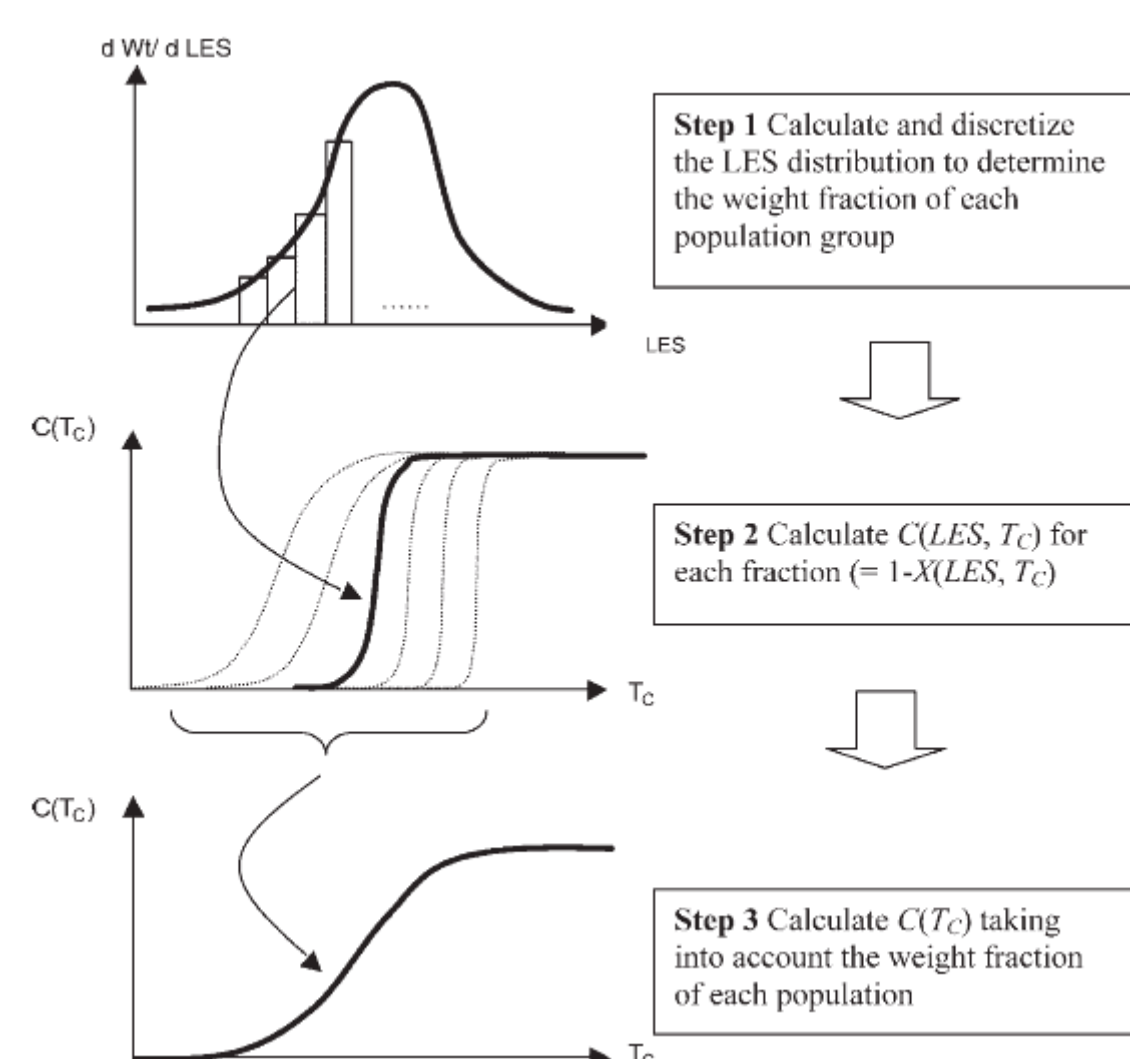**Figure 3:** Illustration of ethylene sequence (ES), longest ethylene sequence (LES) in a copolymer sample

Figure 4: Illustration of the computational steps to simulate integral Crystaf profiles of ethylene/1-olefin copolymers [4]

Gibbs-Thomson:

$$T_d(LES) = A - \frac{B}{LES}$$

Avrami:

$$X(t) = 1 - \exp(-kt^n)$$

Inferring CCD

Calibration curves are conventional approach of transferring Crystaf into CCD that relates average comonomer content to peak crystallization temperature. This method is a tedious experimental approach considering that calibration curves depend strongly on operation conditions.
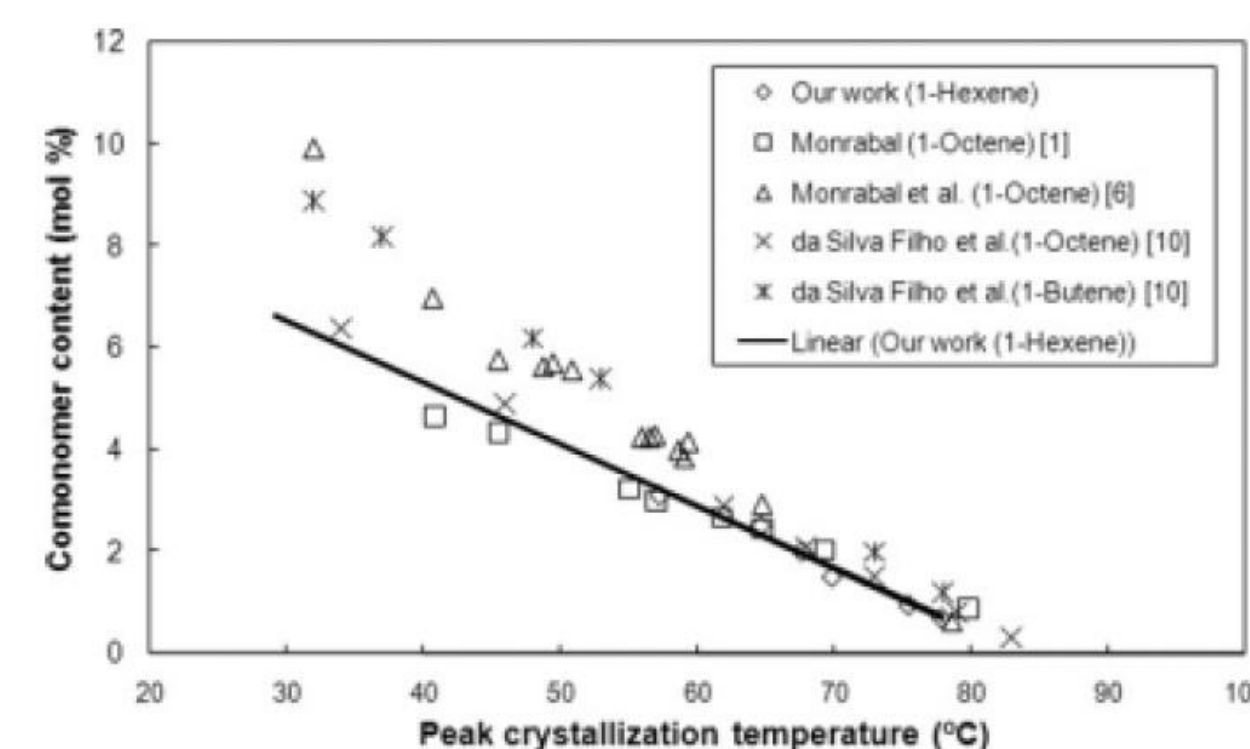

Figure 5: Comparison between Anantawaraskul et al. [4] simulated calibration curves for ethylene/1-hexene and several other calibration curves of other groups at CR = 0.2 $^{\circ}$C/min

Model parameters have different dependencies on operational conditions and samples. We expected the values of n (of Avrami equation) to be relatively constant. Parameter k is dependent on both the cooling rate (CR) and comonomer content (cc), so we therefore defined a heuristic equation for k which has a degree of freedom of three.

$$A = A_1 + A_2.cc$$

$$B = B_1 + B_2.cc + B_3.cc^2$$
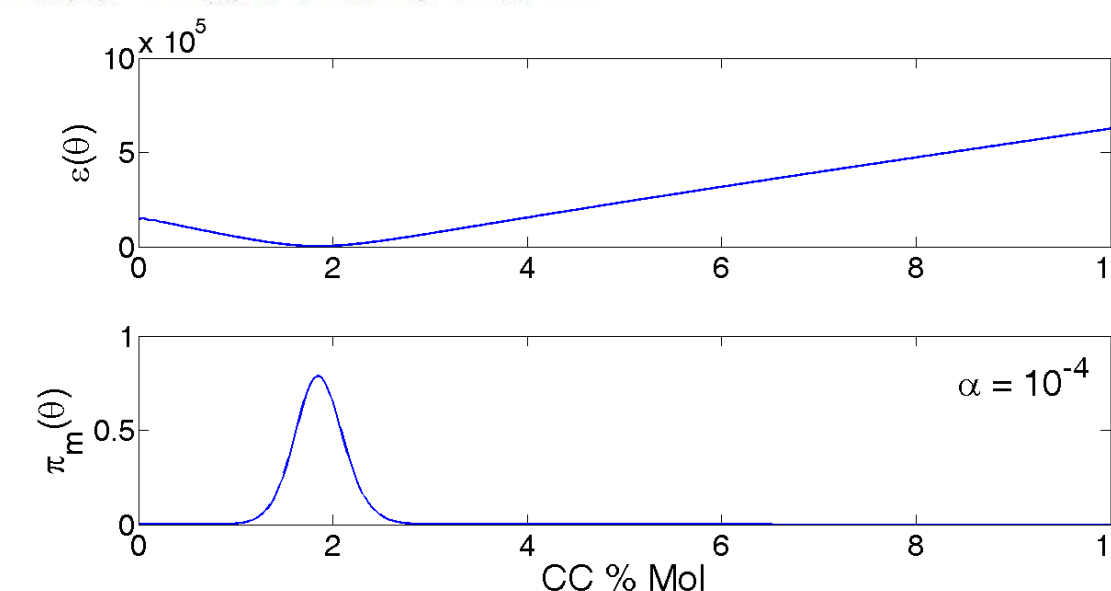
$$\log(k) = \log(k_1 + k_2.cc) + k_3.CR$$

Figure 6: Distance between the modeled and Crystaf profiles for an array of comonomer contents ($CC \in [0,10]$), likelihood function for each CC ($\pi_m = \exp(-\alpha\epsilon(\theta))$)
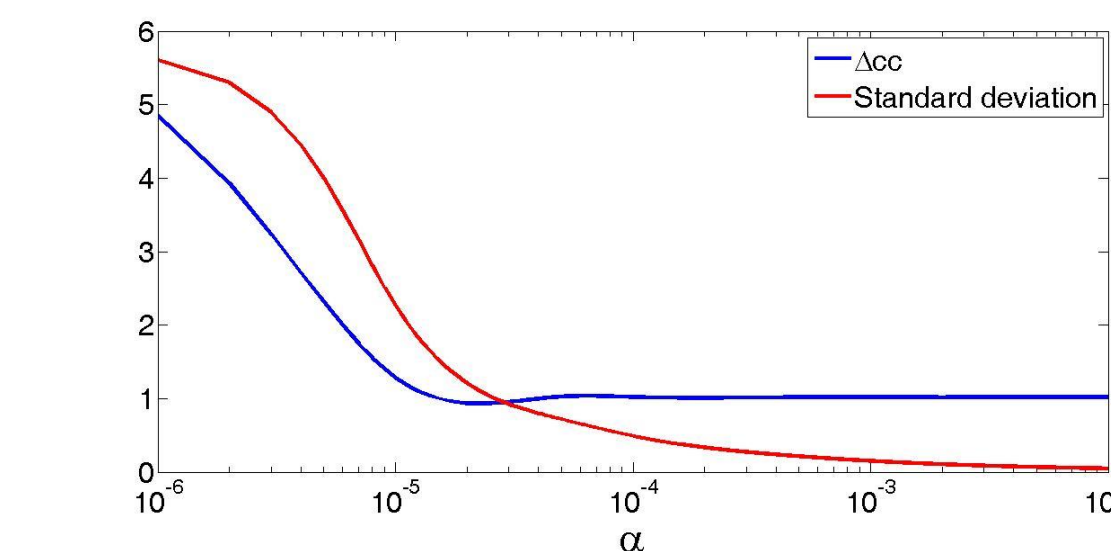

Figure 7: Finding optimum value of α

References

1. B. Monrabal. Crystallization analysis fractionation: A new technique for the analysis of branching distribution in polyolefins. J. Appl. Polym. Sci., 52(4):491-499, 1994
2. Polymer Char Crystaf datasheet
3. S. Anantawaraskul, J. B. P. Soares, and P. M. Wood-Adams. Cocrystallization of blends of ethylene/1-olefin copolymers: An investigation with crystallization analysis fractionation (Crystaf). Macromol. Chem. and Phys., 205(6):771-777, 2004
4. S. Anantawaraskul, P. Jirachaithorn, J. B. P. Soares, and J. Limtrakul. Mathematical modeling of crystallization analysis fractionation of ethylene/1-hexene copolymers. J.Polym. Sci. B: Polym. Phys.,45(9):1010-1017, 2007