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Polymer Analysis Polymer Theory

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Polymer Analysis
Polymer Theory

With contributions by
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Fractionation of Semicrystalline Polymers by Crystallization Analysis Fractionation and Temperature Rising Elution Fractionation

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Abstract Crystallization analysis fractionation (Crystaf) and temperature rising elution fractionation (Tref) are analytical techniques for determining the distribution of chain crystallizabilities of semicrystalline polymers. These techniques fractionate polymer chains on the basis of the differences in their chain microstructures that affect their crystallizabilities in dilute solutions. Both techniques can be used to estimate the chemical composition distribution of copolymers and the tacticity distribution of homopolymers. This information is crucial for understanding polymerization mechanisms and constructing structure–property relationships. This review covers the theoretical aspects of both techniques, describes their basic operation procedures and applications, and discusses the mathematical models proposed for Crystaf and Tref.

Keywords Chemical composition distribution · Composition heterogeneity · Crystallization analysis fractionation · Polyethylene · Polyolefins · Temperature rising elution fractionation

Abbreviations

A-Tref	Analytical temperature rising elution fractionation
CC	Average comonomer content
CCD	Chemical composition distribution
CR	Cooling rate
Crystaf	Crystallization analysis fractionation
DSC	Differential scanning calorimetry
FTIR	Fourier transform IR
HDPE	High-density polyethylene
LDPE	Low-density polyethylene
LLDPE	Linear low-density polyethylene
MWD	Molecular weight distribution
P-Tref	Preparative temperature rising elution fractionation
SEC	Size-exclusion chromatography
SNA	Successive nucleation/annealing
SSF	Successive solution fractionation
Tref	Temperature rising elution fractionation
ΔT_C	Temperature difference between Crystaf peak temperatures

1 Introduction

Polymer microstructural characterization provides information that is essential to understand polymerization mechanisms and to construct structure–property relationships required for the production of polymers with a set of well-defined molecular and macroscopic properties.

Crystallization analysis fractionation (Crystaf) is a recently developed characterization technique that fractionates polymer chains according to their crystallizabilities in a dilute solution [1, 2]. This technique is based on the continuous nonisothermal crystallization of polymer chains from a dilute solution. During crystallization, the concentration of polymer in solution is measured as a function of crystallization temperature, generating a cumulative concentration profile such as the one shown in Fig. 1. The derivative of this cumulative concentration profile is proportional to the fraction of polymer crystallized at each temperature interval and represents the distribution of chain crystallizabilities in the sample.

For ethylene/1-olefin copolymers, chain crystallizability is mainly controlled by the fraction of noncrystallizable comonomer units in the chain. Consequently, the differential Crystaf profile shown in Fig. 1, together with an appropriate calibration curve, can be used to estimate the copolymer chemical composition distribution (CCD), also called the short-chain branch distribution. The CCD of a copolymer describes the distribution of the

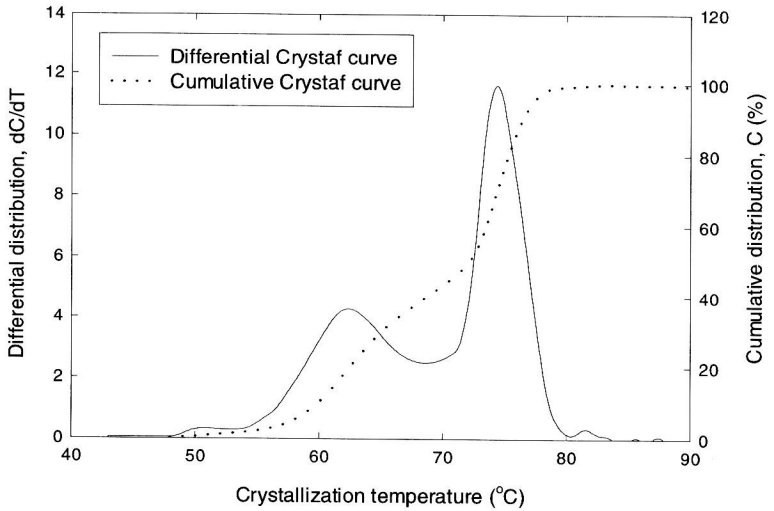

Fig. 1 Cumulative and differential crystallization analysis fractionation (*Crystaf*) profiles of a blend of two polyolefins

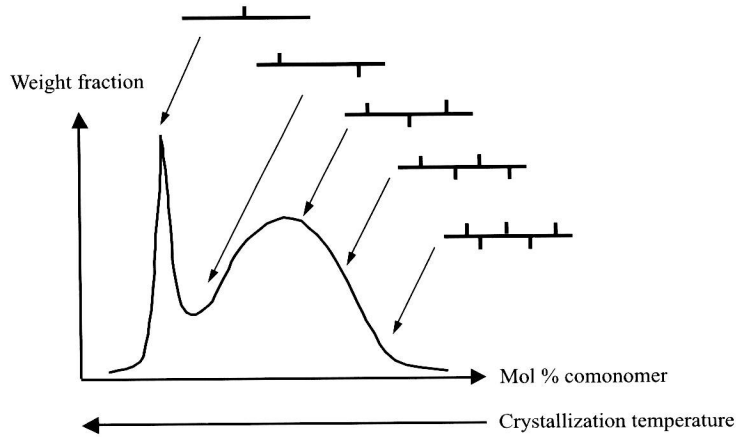

Fig. 2 Chemical composition distribution (*CCD*) of a typical Ziegler–Natta linear low-density polyethylene, reflecting the composition heterogeneity of these copolymers

comonomer fraction in its chains, reflecting its composition heterogeneity (Fig. 2). Composition heterogeneity in copolymers can significantly influence their physical properties. For example, linear low-density polyethylene (LLDPE) with a narrow CCD has much better film properties than LLDPE with a broad CCD [3, 4].

Several factors may contribute to CCD heterogeneity [5]. The more pervasive one is the statistical nature of polymerization which forces the composition of any synthetic copolymer chain to be always distributed around a certain average value. For multi-site-type catalysts, e.g. heterogeneous Ziegler–Natta catalysts, each active site type has a distinct set of polymerization kinetics constants and produces polymer chains with different average microstructures. Therefore, the polymers synthesized with these catalysts are mixtures of chains with different average chain lengths and average comonomer compositions (Fig. 3). Nonuniform polymerization conditions, i.e. temporal and spatial variations in monomer concentration and temperature during polymerization, may also be responsible for CCD heterogeneity. Comonomer compositional drift, a commonly encountered phenomenon in batch and semibatch polymerizations, can significantly broaden the CCD of copolymers.

In the case of stereoregular polymers, such as isotactic and syndiotactic polypropylene, chain tacticity is the main factor affecting crystallizability. Crystaf can also be used to measure the distribution of tacticity. Since the distribution of tacticity is often modeled with pseudo binary copolymerization models (i.e. the meso and racemic insertions stand for the comonomer type in the case of a copolymer), the following discussion for copolymers can be easily modified to describe the tacticity distribution of stereoregular polymers.

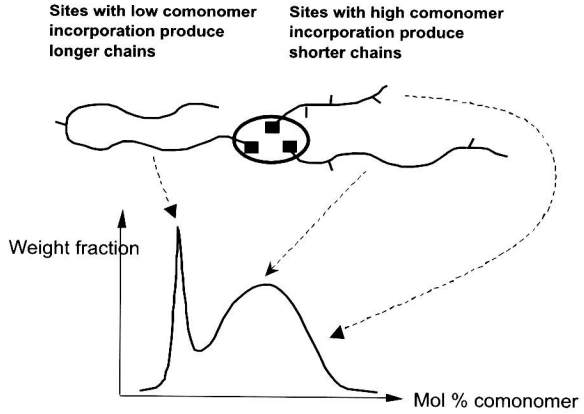

Fig. 3 Copolymers produced by Ziegler–Natta catalysts exhibiting a broad CCD. Chains made by different active sites have different microstructural distributions

Crystaf was developed as an alternative to temperature rising elution fractionation (Tref). Although both techniques are based on similar fractionation mechanisms and provide comparable results, Tref operation tends to be more time-consuming because it involves two fractionation steps, crystallization and elution, while Crystaf requires only the crystallization step. Similarly to Crystaf, the most important fractionation step in Tref occurs during the crystallization step, but data collection in Tref is done only during the elu-

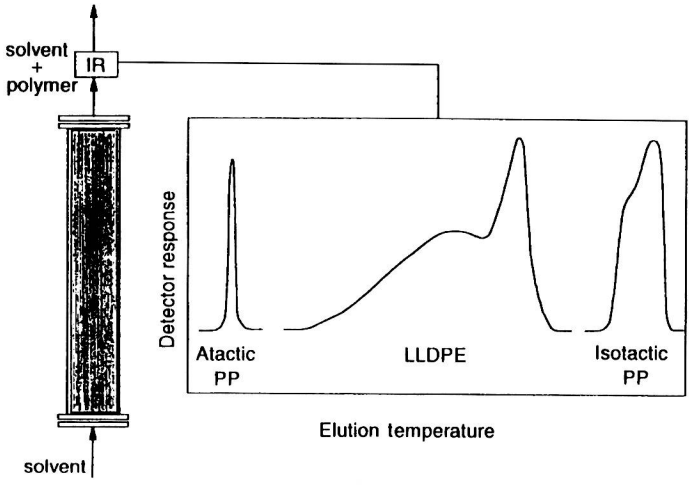

Fig. 4 Elution step of temperature rising elution fractionation (*Tref*) analysis and typical Tref profiles of different polymers [5]. *LLDPE* linear low-density polyethylene, *PP* polypropylene

tion period (Fig. 4). In this review, an overview of Tref operation will also be given and relevant recent research findings related to Tref will be highlighted. More comprehensive reviews focusing solely on Tref are available in the literature [5–9]. This review focuses on the fractionation of ethylene/α-olefin copolymers by Crystaf and Tref, because these techniques have been used more often to analyze this class of polymers. Extensions to other types of semicrystalline polymers, however, will also be discussed when required.

2 Theoretical Background

The fractionation mechanism of Crystaf and Tref relies on differences of chain crystallizabilities in dilute solution: polymer chains with high crystallizabilities will be fractionated at higher temperatures, while chains with low crystallizability are fractionated at lower temperatures. In this section, we review the basic theory of polymer crystallization in dilute solutions to explain how solvent type, polymer volume fraction, molecular weight, and comonomer content affect chain crystallizabilities and equilibrium melting temperatures. The theory describing the CCD of copolymers will also be summarized.

2.1 Thermodynamic Considerations for Homopolymer Solutions

The Flory–Huggins equation for the free energy of mixing can be used to describe the thermodynamic equilibrium of a concentrated polymer solution assuming a uniform distribution of solvent and polymer segments [10, 11]. The decrease in the equilibrium melting temperature of the polymer due to the presence of solvent and the number of chain segments is given by

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \left(\frac{R}{\Delta H_u}\right)\left(\frac{V_u}{V_l}\right)\left[-\frac{\ln(v_2)}{x} + \left(1 - \frac{1}{x}\right)v_1 - \chi_1 v_1^2\right], \quad (1)$$

where T_m^0 is the melting temperature of the pure polymer, T_m is the equilibrium melting temperature of the polymer in solution, ΔH_u is the heat of fusion per repeating unit, V_u and V_l are the molar volumes of the polymer repeating unit and diluent, respectively, v_1 and v_2 are the volume fractions of the diluent and polymer, respectively, x is the number of segments, and χ_1 is the Flory–Huggins thermodynamic interaction parameter.

The crystallization step in Crystaf and Tref, however, occurs in dilute solution. Theoretically, this situation is more complicated because polymer segments are nonuniformly distributed through the solution. Strictly speaking, for dilute solutions the Flory–Huggins free-energy function shown in

Eq. 1 is no longer valid. To account for the nonuniform segment distribution, the general theory for dilute solutions, where the chemical potential of the solvent is expressed in virial form, has to be considered. Fortunately, it has been found that the change in chemical potential of the polymer with increasing dilution is so small that it does not have any appreciable effect on its equilibrium melting temperature [12]. For practical purposes, Eq. 1 is obeyed over the complete concentration range of dilutions.

To examine the effect of chain length on the melting temperature of a polymer in a dilute solution, it is appropriate to rearrange Eq. 1 as follows:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u}\frac{V_u}{V_1}\left(v_1 - \chi_1 v_1^2\right) - \frac{R}{\Delta H_u}\left[\frac{\ln\left(v_2\right)}{r} + \frac{v_1}{r}\right]. \tag{2}$$

Here, the number of repeating units per polymer chain (r) is used instead of the number of segments (x). The second term on the right-hand side quantifies the effect of chain length, indicating that the equilibrium melting temperature decreases with a reduction in molecular weight [13]. However, this term is only important for chains with low molecular weights, as clearly

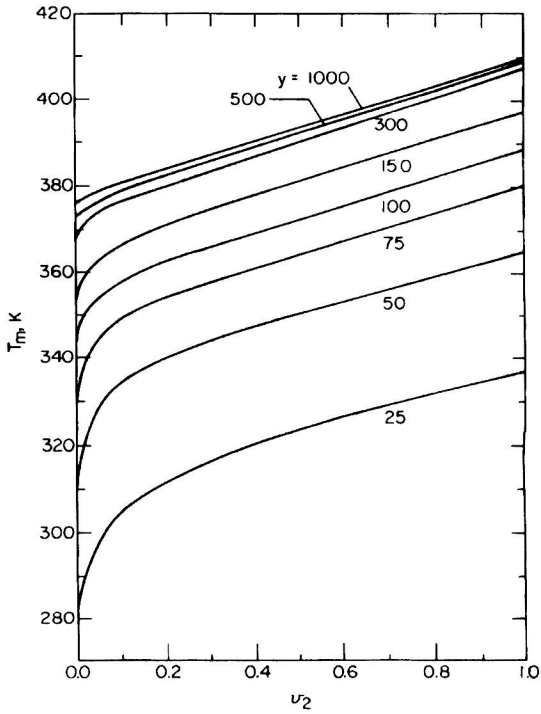

Fig. 5 Predicted melting temperatures for several chain lengths using Eq. 2 [13]

illustrated in Fig. 5. For large values of r, the case of polymers with high molecular weight, the melting temperature is relatively independent of chain length and Eq. 2 is reduced to the simpler form

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u}\frac{V_u}{V_1}\left(v_1 - \chi_1 v_1^2\right) . \tag{3}$$

Equation 3 implies that all polymer chains having reasonably large molecular weights will crystallize at the same temperature, all other factor being the same. In other words, the effect of molecular weight on Crystaf or Tref profiles of high molecular weight polymers should be negligible. This is in good agreement with experimental observations for both Crystaf and Tref [14, 24].

2.2 Thermodynamic Considerations for Copolymer Solutions

In the case of copolymer solutions, the melting temperature also depends on interactions between the different monomeric units and the solvent. Considering the case in which the crystalline phase is pure (i.e., only monomeric units of a single type crystallize and no solvent is present in the lattice), the decrease in the melting temperature can be derived in a similar manner as for the homopolymer solution case using the Flory–Huggins theory with an appropriate modification [15]. To take into account the interactions between both comonomers and solvent, the net interaction parameter for binary copolymers should be calculated as follows:

$$\chi_1 = v_A\chi_{1A} + v_B\chi_{1B} - v_A v_B\chi_{AB} , \tag{4}$$

where χ_1 is the interaction parameter of a binary copolymer with pure solvent, χ_{1A} and χ_{1B} are the interaction parameters of the corresponding homopolymers with the solvent, χ_{AB} is the interaction parameter between comonomers A and B in the copolymer chain, and v_A and v_B are the volume fractions of comonomers A and B in the copolymer molecules, respectively.

If the steric structures of both comonomer units in random copolymers are similar, the melting temperature depression equation will be the same as Eq. 1, with the interaction parameter calculated with Eq. 4. For a given copolymer, the crystallizabilities of copolymer chains in dilute solution strongly depend on the chain composition. From thermodynamic considerations, this can be explained from the fact that changes in copolymer composition alter the value of the interaction parameter defined by Eq. 4. For copolymers with two chemically similar comonomers, χ_{1A} will be very close to χ_{1B}, and χ_{AB} will approach zero. In this system, one can simply use Eq. 1 with $\chi_1 = \chi_{1A} \approx \chi_{1B}$.