Macromolecular Symposia Vol. 257

Polyolefin Characterization

Selected Contributions
from the conference:
The First International Conference on
Polyolefin Characterization (ICPC)
Houston, TX (USA), October 16–18, 2006

Symposium Editor:
João B. P. Soares
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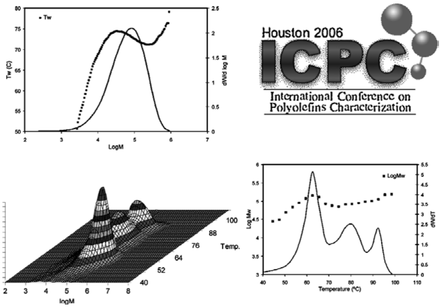
Cover: Tridimensional surface plot of a multiple-reactor polyethylene sample measured with TREF-GPC cross-fractionation (lower left corner) and its two-dimensional projections showing the MWD and average TREF elution temperature as a function of molecular weight (upper left corner) and TREF profile and log M_w as a function of elution temperature (lower right corner).



Polyolefin Characterization

Houston, TX (USA), October 16-18, 2006

The final properties and applications of polyolefins are determined by their microstructures. This statement can be made for any polymer, but it is even more relevant for polyolefins since they are composed of such simple building blocks. Therefore, it is no surprise that the study of polyolefin microstructure has always been an essential part of catalyst research, process troubleshooting and optimization, and product development. In addition to conventional Ziegler-Natta polyolefins, which already have rather intricate microstructures, there is a rapidly growing interest in producing polyolefins with increasingly more complex molecular architectures, using combinations of single and multiple-site catalysts and/or polymerization processes with two or more reactors operated in series at different conditions. Recent examples are linear-block and branch-block copolymers with elastomeric properties, copolymers with long chain branches made by one or more single-site catalysts, and bimodal resins made in tandem or multizone reactor processes. The increasing sophistication of catalyst systems and polymerization processes can only be fully realized in practice if efficient and easy to use polyolefin characterization techniques are available. The First International Conference on Polyolefin Characterization (ICPC) was organized to fill this important industrial and academic need, providing a discussion forum on the characterization and fractionation techniques of polyolefins.

The first ICPC took place in Houston, TX, from October 16 to 18, 2006. One hundred and seven participants from 18 different countries attended the conference: 65 from the industry, 24 from academia, and 18 from vendor companies. The strong participation from the polymer manufacturing industry from North America, Europe and Asia shows the industrial relevance and need of such a conference. In addition, a one-day course on polyolefin characterization techniques was offered before the beginning of the conference for those participants interested in an update on the principles of gel permeation chromatography (GPC), temperature rising elution fractionation (TREF), and crystallization analysis fractionation (CRYSTAF).

The oral presentations given during the 1st ICPC were divided according to main topic areas into Separation and Fractionation, High Throughput, Thermal and Crystallinity Analysis, Spectroscopy, and Rheology. In addition to the oral presentations, 29 posters were displayed.

We intend to continue organizing the ICPC biannually, alternating between North American and European locations. The 2nd ICPC will take place in September 2008 (exact dates are still to be defined) in Valencia, Spain. Readers interested in being included in the conference's mailing list are welcome to send us their requests by e-mail to *raquel.ubeda@icpc-conference. org*

João B. P. Soares

ICPC organizing committee members: Benjamin Monrabal, Raquel Ubeda, Colin Li Pi Shan, and João B. P. Soares.

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An Overview of Important Microstructural Distributions for Polyolefin Analysis

João B.P. Soares

Summary: Polyolefins with complex microstructures are becoming increasingly common in academic and industrial applications. Polyolefin analytical techniques are evolving to provide a more detailed picture of these microstructures, with the development and improvement of hyphenated-techniques and cross-fractionation methods. These modern analytical techniques provide a wealth of information on polyolefin microstructure and, despite being extremely useful, they can also be hard to interpret without the help of mathematical models that link polymerization kinetics to chain microstructure and polymer characterization results. In this paper we review some of the most important distributions for polyolefin microstructure and derive a few new expressions that help understand the results obtained with several polyolefin characterization techniques.

Keywords: polyethylene; polymer characterization; polymer fractionation; polymer microstructure; polyolefins

Introduction

The remarkable versatility of polyolefins come from the fact that ethylene, propylene and α-olefins can be copolymerized to create polymer chains with microstructures that lead to very different physical properties.

Polyolefin properties are ultimately defined by the way the monomers are connected to form linear and branched polymer chains with different degrees of regularity. It is, therefore, very important to characterize the microstructure of polyolefins and to quantify this microstructure using fundamental models.

In this short overview, we will present some important equations that describe polyolefin microstructure and discuss some modeling principles that can be used to help understand the results obtained with several polyolefin characterization techniques.

Distribution of Chain Length, Chemical Composition, and Long Chain Branching

The most general distribution for the microstructure of polyolefins made with coordination catalysts is given by the equation:[1,2]

$$w(r,F,i) = \frac{1}{(2i+1)!} r^{2i+1} \tau^{2i+2} \exp(-r\tau)\sqrt{\frac{r}{2\pi\beta}} \exp\left[-\frac{r(F-\overline{F})^2}{2\beta}\right] \tag{1}$$

In Equation (1), $w(r,F,i)$ is the height of the weight distribution for chains of length r, comonomer fraction F, and i long chain branches (LCB) per chain. This equation has only two parameters, β and τ, defined as:

$$\beta = \overline{F}(1-\overline{F})\sqrt{1-4\overline{F}(1-\overline{F})(1-r_1 r_2)} \tag{2}$$

$$\tau = \frac{\textit{rate of transfer} + \textit{rate of LCB formation}}{\textit{rate of propagation}} \tag{3}$$

Finally, $\overline{F}$ is the average fraction of comonomer in the copolymer (as calculated

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from Mayo-Lewis equation, for instance) and r_1 and r_2 are the comonomer reactivity ratios.

This equation was derived based on the mechanism widely accepted for olefin polymerization with coordination catalysts where chains can propagate by monomer insertion, terminate through several transfer mechanism, and LCBs are formed by the incorporation of vinyl-terminated polymer chains, commonly called macromonomers. No other assumption were needed for model development.[1,2]

It is interesting to point out that Equation (1) becomes Stockmayer distribution for linear chains, that is, for $i = 0$:[3]

$$w(r,F) = r\tau^2 \exp(-r\tau)\sqrt{\frac{r}{2\pi\beta}}\exp\left[-\frac{r(F-\overline{F})^2}{2\beta}\right] \tag{4}$$

In addition, if we integrate Equation (4) over all comonomer compositions we obtain Flory's most probable chain length distribution (CLD):[4,5]

$$w(r) = \int_{-\infty}^{\infty} w(r,F)\mathrm{d}(F-\overline{F}) = r\tau^2\exp(-r\tau) \tag{5}$$

For linear chains, the parameter τ is the reciprocal of the number average chain length, r_n:

$$\tau = \frac{\textit{rate of transfer}}{\textit{rate of propagation}} = \frac{1}{r_n} \tag{6}$$

Therefore, in the same way that Stockmayer's distribution is the extension of Flory's distribution to binary copolymers, Equation (1) is the extension of Stockmayer's distribution to non-linear copolymers. We will now start applying Equation (1), (4), and (5) to several common polyolefin characterization techniques.

Molecular Weight Distribution of Linear Chains

Molecular weight distributions (MWD) of polyolefins made with single site catalysts follow Flory's most probable distribution, Equation (5). MWDs are usually measured with high-temperature gel permeation chromatography (GPC) and expressed in log scale. Before we can use Equation (5) to describe the experimental MWD of polyolefins, we need to apply two simple mathematical transformations. First, we need to change the CLD into a MWD using the relation,

$$w(MW)\mathrm{d}MW = w(r)\mathrm{d}r \tag{7}$$

where MW is the polymer molecular weight. Since $\mathrm{d}MW/\mathrm{d}r$ equals the molar mass of the repeating unit in the polymer chain (mw), Equation (5) becomes,

$$w(MW) = MW\hat{\tau}^2\exp(-MW\hat{\tau}) \tag{8}$$

where,

$$\hat{\tau} = \frac{\tau}{mw} = \frac{1}{r_n \cdot mw} = \frac{1}{M_n} \tag{9}$$

and M_n is the number average molecular weight of the polymer.

Equation (8) must now be rendered in log scale through the transformation:

$$w(\log MW)\mathrm{d}\log MW = w(MW)\mathrm{d}MW \tag{10}$$

Consequently:

$$w(\log MW) = 2.3026 \times MW^2\hat{\tau}^2\exp(-MW\hat{\tau}) \tag{11}$$

Figure 1 shows that the MWD of a polyethylene sample made with two metallocene catalysts supported on the same silica carrier is well represented by the superposition of two Flory's distributions. Since we have two single-site catalysts in Figure 1, the MWD of the combined polymer, $W(\log MW)$ is described by the weighed sum of two Flory's distributions,

$$W(\log MW) = m_{Zr}w(\log MW)_{Zr} + (1-m_{Zr})w(\log MW)_{Hf} \tag{12}$$

where m_{Zr} is the mass fraction of polyethylene produced by the zirconium catalyst.

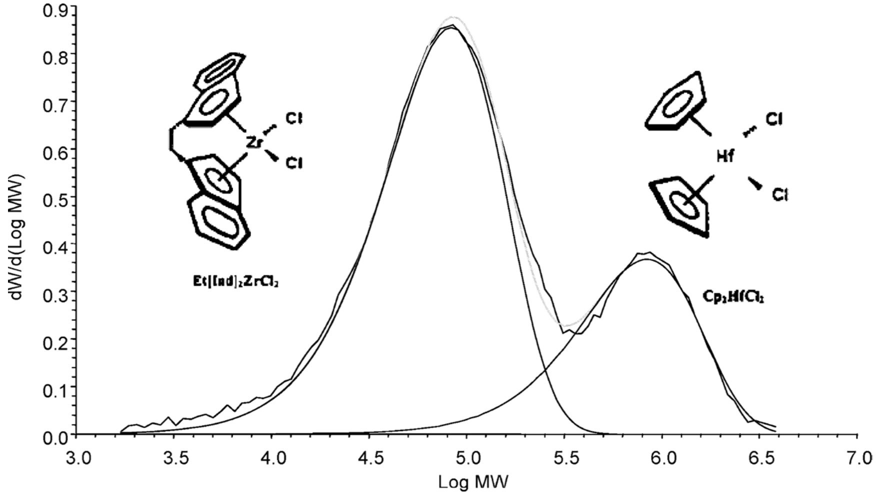


Figure 1.
Comparison of the GPC-measured MWD of a polyethylene sample made with two metallocenes supported on silica and model prediction using Flory's distribution. The peaks for polymer made with both metallocenes are described with Equation (8).[6]

This modeling concept is commonly extended to catalysts that have more than one site type, such as heterogeneous Ziegler-Natta and Phillips catalysts.[7] Figure 2 shows an example of such a MWD representation for the case of a polyethylene resin made with a heterogeneous Ziegler-Natta catalyst.

Therefore, we can generalize Equation (12) for the case of a catalyst with *n*

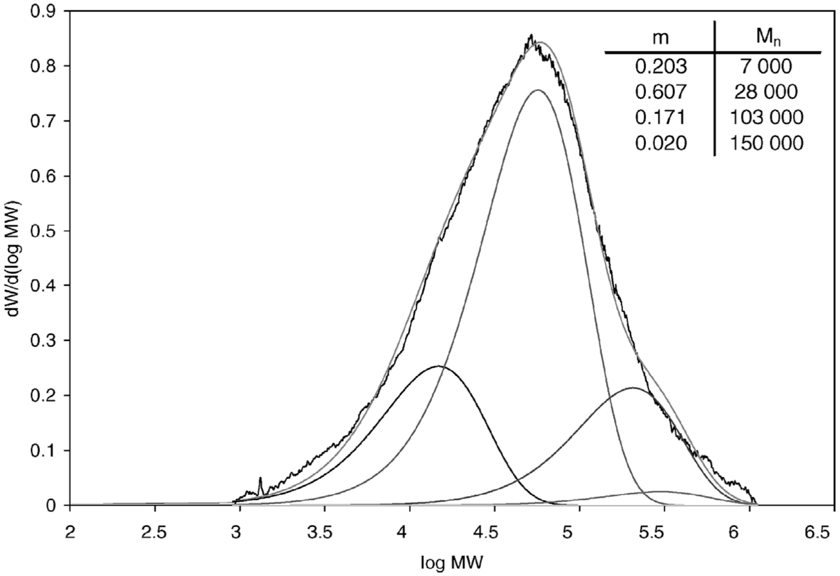


Figure 2.
MWD of a polyethylene sample made with a heterogeneous Ziegler-Natta catalyst. The MWD is represented as a superposition of four Flory's distributions, having the mass fractions (*m*) and number average molecular weights (M_n) indicated in the table.

different site types:

$$W(\log MW) = \sum_{j=1}^{n} m_j w_j(\log MW)$$
$$= 2.3056 \times MW^2 \sum_{j=1}^{n} m_j \hat{\tau}_j^2 \exp(-MW\hat{\tau}_j) \qquad (13)$$

Equation (13) is a statement of our first modeling principle:

Principle 1: The microstructural distribution of a polymer made with a multiple-site catalyst can be represented as a weighted superposition of distributions for single-site catalysts.

This principle must be used with care: we must keep in mind that it only provides a convenient way to represent microstructural distributions of polymers made with multiple site catalysts.

Hyphenated Techniques: GPC-IR

The use of a infrared detector (IR) with GPC is becoming increasingly popular for polyolefin characterization. This relatively simple combination permits the detection of the average chemical composition (generally reported as molar fraction of α-olefin or short chain branching frequency) as a function of molecular weight. Figure 3 shows the GPC-IR plot for a linear low density polyethylene (LLDPE) resin. We immediately notice the fingerprint mark of a heterogeneous Ziegler-Natta catalyst: as the molecular weight increases, the fraction of 1-butene in the sample decreases.

It is possible to use Modeling Principle 1 to interpret this profile. Figure 4 shows that the MWD can be represented as a superposition of five Flory's distributions. If we assume that each distribution is associated with an active site type that produces LLDPE with a distinct average molar fraction of 1-butene (F_j), we can say that the overall 1-butene fraction measured by the IR detector in a given molecular weight (ΔMW) interval is,

$$F(\Delta MW) = \sum_{j=1}^{5} \Delta w_j(\Delta MW) F_j \qquad (14)$$

where Δw_j is the mass fraction of polymer made on site type j eluting from the GPC column set in the interval ΔMW. The mass fractions Δw_j are obtained from the integration of the Flory distribution associated with each site type:

$$\Delta w_j(MW) = m_j \int_{MW}^{MW+\Delta MW} w_j(MW)\mathrm{d}MW$$
$$= m_j \left\{ \begin{array}{c} (1 + MW\hat{\tau}_j)\exp(-MW\hat{\tau}_j) \\ -[1 + (MW + \Delta MW)\hat{\tau}_j] \\ \exp[-(MW + \Delta MW)\hat{\tau}_j] \end{array} \right\} \qquad (15)$$

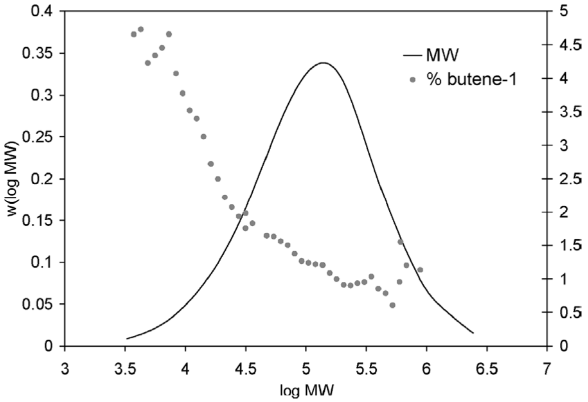
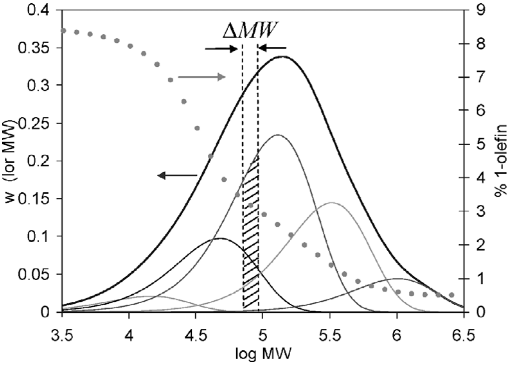


Figure 3.
GPC-IR plot of a LLDPE resin.



m	M_n	F
0.0382	7 000	0.09
0.18	24 000	0.04
0.433	65 000	0.03
0.2674	164 000	0.01
0.0815	510 000	0.005

Figure 4.

GPC-IR representation using five site types. The table lists the mass fractions (*m*), number average molecular weights (M_n), and 1-olefin fraction (*F*) of polymer made on each site type.

Notice that for the low molecular weight region, one may have to account for the effect of methyl end groups on the experimental IR data.

This simple representation of GPC-IR profiles permit a systematic interpretation of results observed in several academic and industrial polyolefin analytical laboratories.

Chemical Composition Distribution of Linear Chains

The bivariate distribution of chain length and chemical composition of linear polyolefins is given by Stockmayer's distribution, Equation (4). A short description of its main features is useful to clarify several properties of binary copolymers such as LLDPE and propylene/ethylene copolymers.

Figure 5 shows Stockmayer's distributions for four model single-site polyolefins with the same reactivity ratio product ($r_1r_2 = 1$, random copolymers) and average ethylene fraction ($\overline{F} = 0.8$), but with different average chain lengths. Notice that, as the number average chain lengths of the samples increase, their distributions become narrower on the chemical composition dimension. This trend is also observed for each sample individually: shorter chains have a broader chemical composition distribution (CCD) than longer chains. This is a well known effect, caused by the statistical averaging of the chemical compositions per chain as the chains get longer. Samples with infinite length would all have comonomer fractions exactly equal to the average comonomer fraction of the polymer.

The other important property of Stockmayer's distribution is shown in Figure 6: the CCD component broadens steadily when the reactivity ratio product increases, that is, as the copolymer passes from alternating to random and, finally, to block comonomer sequences. This is also an intuitive concept, since all chains of a perfectly alternating copolymer have the same composition ($F = 0.5$), while a tendency to form long blocks of one of the comonomer will necessary increase intermolecular heterogeneity.

We can apply our Modeling Principle 1 to Stockmayer's distribution to describe the bivariate distribution of chain length (or molecular weight) and chemical composition of polyolefins made with multiple site catalysts. In this case, the following generic expression applies,

$$W(r,F) = \sum_{j=1}^{n} m_j w_j(r,F) \tag{16}$$

where $w_j(r,F)$ for each site is given by Equation (4). It should be clear that this equation can be transformed into a molecular weight distribution and expressed in either linear or log scale, using the transformations demonstrated above for Flory's distribution.

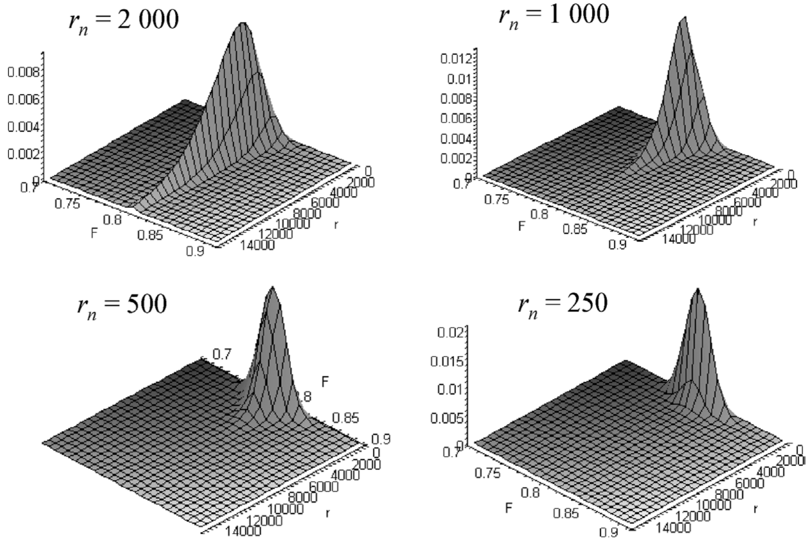


Figure 5.
CLD and CCD of four model single-site polyolefin with different number average chain lengths, r_n. Model parameters: $\bar{F} = 0.8$, $r_1 r_2 = 1$, and $\tau = 1/r_n$.

Figure 7 illustrates two bivariate distributions for LLDPE resins. The experimental distribution on the left side was measured using Polymer C*h*ar CFC 300, a cross fractionation instrument that combines fractionation by temperature rising elution fractionation (TREF) and GPC,[8] while the distribution on the right side of the figure is a model representation using Equation (16) for a three site-type catalyst.

Very few polyolefin characterization laboratories have cross-fractionation instruments available, but most have either a TREF and/or a crystallization analysis fractionation (Crystaf) unit. We can obtain the CCD component of Stockmayer's distribution with the integration:

$$w(F) = \int_0^\infty w(r,F)\mathrm{d}r = \frac{3}{4\sqrt{2\beta\tau}\left[1 + \frac{(F-\bar{F})^2}{2\beta\tau}\right]^{5/2}} \tag{17}$$

We will use Equation (17) to help us define our second modeling principle:

Principle 2: Individual microstructural distributions can be obtained from the integration of multivariate distributions.

Notice that we had already used Modeling Principle 2 to isolate the CLD component, Equation (4), from Stockmayer's distribution.

Figure 8 shows how the breadth of the CCD depends on the product of the parameters β and τ. The distribution broadens as the polymer chains become shorter (increasing τ) or the copolymer chains become blockier (increasing β). These trends had already been described in Figure 5 and 6, and appear now as part of a lumped parameter given by the product $\beta\tau$. Figure 8 captures the essence of olefin copolymer microstructure in a very elegant plot.

Similarly to the procedure we adopted to describe the MWD of polyolefins made with multiple-site catalysts, the CCD of polyolefins made with these catalysts can be represented as a weighted superposition of single-site CCDs:

$$W(F) = \sum_{j=1}^{n} m_j w_j(F) \tag{18}$$

The MWD and CCD (measured as TREF elution profiles) of an ethylene/1-butene copolymer made with a heterogeneous Ziegler-Natta catalyst is shown in

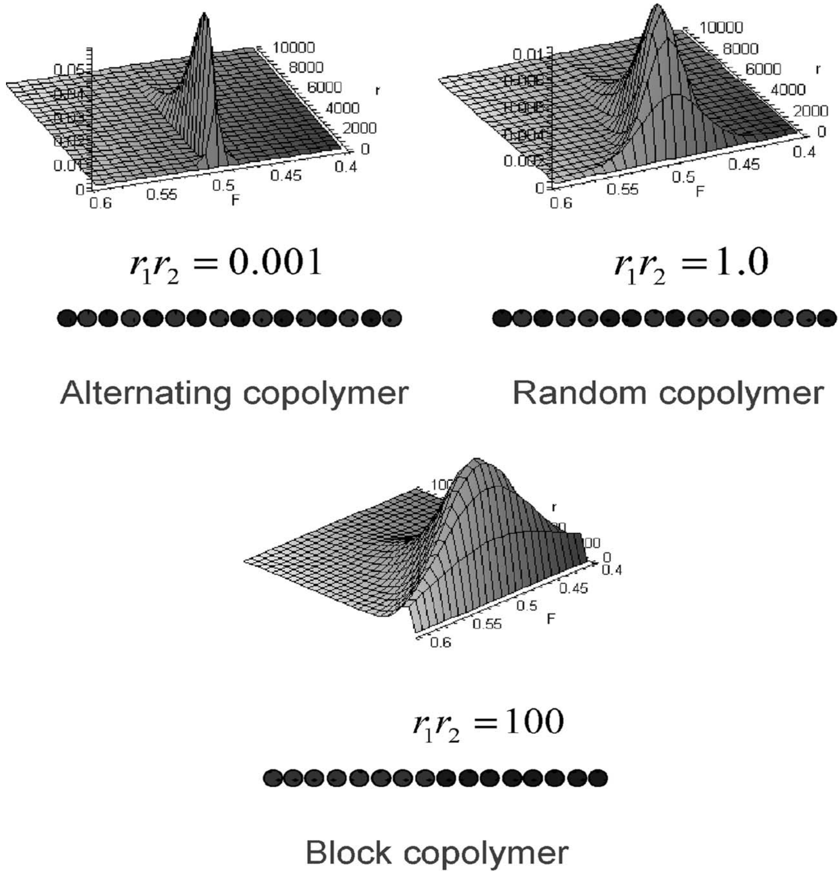


Figure 6.

CLD and CCD of three model single-site polyolefin with different reactivity ratio products, r_1r_2. Model parameters: $\bar{F} = 0.5$, $\tau = 0.001$.

Figure 9. Both profiles can be well represented with four site types. It should be noticed, however, that TREF and Crystaf profiles are related to, but are not in fact the CCD described by Equation (17). Therefore, the mathematical treatment illustrated in Figure 9 is only a first over simplified approximation. The development of fundamental models for TREF and Crystaf is a hard subject that is beyond the scope of this short review.[9,10]

Hyphenated Techniques: TREF-LS

When a light-scattering detector is added to TREF, it is possible to measure the weight average molecular weight (M_w) of polyolefin as a function of elution temperature or comonomer fraction. This technique provides a complementary analysis to the other hyphenated technique, GPC-IR, described above. Similar information can also obtained by projecting the CFC results onto the TREF elution temperature plane and computing the M_w for each elution temperature.

Figure 10 shows one analytical result for an ethylene/α-olefin copolymer with rather complex microstructure. We notice that there is a strong correlation between the elution temperature (or comonomer fraction) and the weight average molecular weigh of the polymer. The trends for the