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Block Index for Characterizing Olefin Block Copolymers

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Summary: Olefin block copolymers produced by chain shuttling catalysis exhibit crystallinity characteristics that are distinct from what would be expected for typical random olefin copolymers with comparable monomer compositions produced from either 'single-site' or heterogeneous catalysis. Olefin block copolymers produced by chain shuttling catalysis have a statistical multiblock architecture. A unique structural feature of olefin-based block copolymers is that the intra-chain distribution of comonomer is segmented (statistically non-random). Fractionating an olefin block copolymer by preparative temperature rising elution fractionation, TREF, results in fractions that have much higher comonomer content than comparable fractions of a random copolymer collected at an equivalent TREF elution temperature. We have developed a "block index" methodology which quantifies the deviation from the expected monomer composition versus the analytical temperature rising elution fractionation, ATREF, elution temperature. When interpreted properly, this index indicates the degree to which the intra-chain comonomer distribution is segmented or blocked. The unique crystallization behavior of block copolymers determine the magnitude of the block index values because the highly crystalline segments along an otherwise non-crystalline chain tend to dominate the ATREF (and DSC) temperature distributions.

Keywords: ATREF; DSC; ethylene-alpha olefin copolymer; olefin block copolymer; random copolymer; TREF

Introduction

The recent break-through in chain shuttling catalyst technology has enabled the production of novel linear olefin multi-block copolymers via coordination catalysis in Dow's continuous solution process. The chain shuttling technology is based on two catalysts with varying comonomer incorporation capabilities and a shuttling agent which transfers a growing polymer chain from a good comonomer incorporator catalyst site to a poor comonomer incorporator catalyst site in a reversible manner. The good comonomer incorporator makes the soft (or non-crystallizing) segments and the poor comonomer incorporator makes the hard (or crystallizing) segments of the block copolymer. The polymerization and properties of these olefin block copolymers (OBCs) have been reviewed recently.[1,2]

This new type of olefin block copolymer is constructed from hard block segments that are rich in ethylene and soft block segments that have α-olefin comonomer along the same polymer chain. These block copolymers have relatively narrow MWD (M_w/M_n $\sim$2) and contain multiple block segments that arise from statistical addition. The number and length of block segments are controlled by the concentration of chain shuttling agent present during the polymerization. In addition to controlling the overall density and melt index of the copolymers, the amount and composition of the segments can be controlled

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to tailor-make materials for specific applications.[3]

Figure 1 provides an example of the hypothetical microstructure of an OBC produced by chain shuttling catalysis. This type of block copolymer can be termed a ‘‘linear statistical multiblock’’ or LSMB and is quite different than the conventional block copolymers made by living polymerization chemistry as well as commercially available polyolefins. In a LSMB the chain lengths, comonomer distribution, and block distribution of block sizes and lengths are polydisperse. By contrast, the traditional block copolymers have structures that are well-controlled to be nearly mono-disperse (equal chain lengths) and the lengths of each type of block are essentially equal from chain to chain as dictated by the polymerization chemistry and conditions.

For typical random polyolefins, the molecular structure distributions such as the molecular weight distribution and/or the short chain branching distribution can be measured by GPC and ATREF/CRYSTAF, respectively. However, neither of these techniques is able to measure the blockiness of a copolymer (without prior knowledge of its structure), as reflected in the intrachain monomer distribution. To our knowledge, there are no analytical tools in the literature to specifically characterize an olefin block copolymer.

In this paper, we describe some of the unique analytical characteristics of an olefin block copolymer. In addition, based on deviations from the observed relationship for structure and ATREF elution temperature for random copolymers, we outline a ‘‘Block Index’’ method to quantify the observed microstructure and distinguish it from traditional random copolymers.

Experimental Part

Materials

An olefin block copolymer synthesized by the chain-shuttling method was produced in a continuous polymerization process as described by Arriola et al.[2] The olefin block copolymer was produced using ethylene and 1-octene comonomer as per the design shown in Table 1.

Material Analysis

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry was performed on a TA Instruments Q1000 DSC equipped with an RCS cooling accessory and an auto sampler. A nitrogen purge gas flow of 50 ml/min was used. The sample was pressed into a thin film and melted in the press at about 190 °C and then air-cooled to room temperature (25 °C). About 3–10 mg of material was then cut, accurately weighed, and placed in a light aluminum pan (ca. 50 mg) which was later crimped shut. The thermal behavior of the sample was investigated with the following temperature profile: the sample was rapidly heated to 190 °C and held isothermal for 3 minutes in order to remove any previous thermal history. For these octene-based polymers, the sample was then cooled to −40 °C at 10 °C/min cooling rate and held at −40 °C for 3 minutes. The sample was then heated to 150 °C at 10 °C/min heating rate. The cooling and second heating curves were recorded.

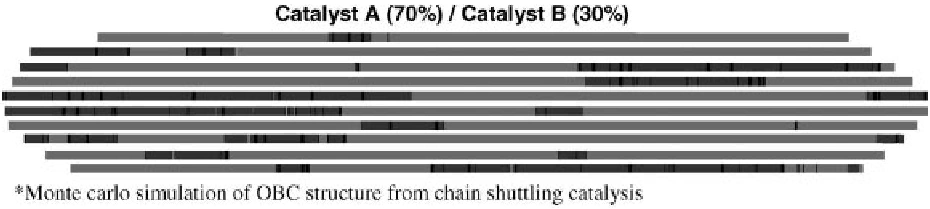


Figure 1.
A pictorial example of a linear statistical multiblock copolymer.

Table 1.
Design of a olefin block copolymer.

Example	Density (g/cc)	I2 (g/min)	wt% Hard Segment or polymer in blend	Targeted* wt% Octene Hard Segment or polymer in blend	Targeted* wt% Soft Segment or polymer in blend	Targeted* wt % Octene in Soft Segment or polymer in blend	Chain Shuttling Agent Present
OBC	0.8786	1.5	29	0.4	71	15	Yes
In Reactor Blend	0.8895	0.9	39	0.4	61	15	No

* As controlled by the polymerization conditions via predictive reactor modelling.

Analytical Temperature Rising Elution Fractionation (ATREF)

In ATREF analysis, the composition to be analyzed was dissolved in 1,2,4 trichlorobenzene (2 mg/ml) at 160 °C and allowed to crystallize in a column containing an inert support (stainless steel shots) by slowly reducing the temperature to 20°C, at a rate of −0.1 °C/min, where the temperature was held for one hour. The instrumentation was equipped with an IR4 infra-red detector (PolymerChar, Valencia, Spain). An ATREF chromatogram curve was then generated by eluting the crystallized polymer sample (at a flow rate of 1 cc/min) from the column while slowly increasing the temperature of the column and eluting solvent (trichlorobenzene) from 20 to 120°C (at a rate of 1.0°C/min).

^{13}C Nuclear Magnetic Resonance (NMR) Analysis

The samples were prepared by adding approximately 3 g of a 50/50 mixture of tetrachloroethane-d^2/orthodichlorobenzene to 0.4 g sample in a 10 mm NMR tube. The samples were then dissolved and homogenized by heating the tube and its contents to 150 °C. The data was collected using a JEOL Eclipse™ 400 MHz spectrometer or a Varian Unity Plus™ 400 MHz spectrometer, corresponding to a ^{13}C resonance frequency of 100.5 MHz. The data was acquired using 4000 transients per data file with a 6 second pulse repetition delay. To achieve maximum signal-to-noise for quantitative analysis, multiple data files were added together. The spectral width was 25,000 Hz with a minimum file size of 32K data points. The samples were analyzed at 130 °C in a 10 mm broad band probe. The comonomer incorporation was determined using the method reported by Zhou et al.[4]

Polymer Fractionation by TREF

Large-scale TREF fractionation was carried out by dissolving 15–20 g of polymer in 2 liters of 1,2,4-trichlorobenzene (TCB) by stirring for 4 hours at 160 °C. The polymer solution is forced by 15 psig (100 kPa) nitrogen onto a 3 inch by 4 foot (7.6 cm × 121.9 cm) steel column packed with a 60:40 (v:v) mix of 30–40 mesh (600–425 μm) spherical, technical quality glass beads (available from Potters Industries, HC 30 Box 20, Brownwood, TX, 76801) and stainless steel, 0.028″ (0.7mm) diameter cut wire shot (available from Pellets, Inc. 63 Industrial Drive, North Tonawanda, NY, 14120). The column is immersed in a thermally controlled oil jacket, set initially to 160 °C. The column is first cooled ballistically to 125 °C, then slow cooled to 20 °C at 0.04 °C per minute and held for one hour. Fresh TCB is introduced at about 65 ml/min while the temperature is increased at 0.167 °C per minute. Approximately 2000 ml portions of eluant from the preparative TREF column are collected in a 16-station, heated fraction collector. The polymer is concentrated in each fraction using a rotary evaporator until about 50 to 100 ml of the polymer solution remains. The concentrated solutions are allowed to stand overnight before adding excess methanol, filtering, and rinsing (approx. 300–500 ml of methanol including the final rinse). The filtration step is performed on a 3 position vacuum assisted filtering station using 5.0 μm polytetrafluoroethylene coated filter paper (available from Osmonics Inc., Cat# Z50WP04750). The filtered fractions are dried overnight in a vacuum oven at 60 °C and weighed on an analytical balance before further testing.

Results and Discussion

Figure 2 shows that olefin block copolymers produced by chain shuttling catalysis have a relatively constant melting-point-versus-density relationship. Karande et al.[3] have shown that OBCs exhibit elastomeric character while still retaining a high melting point (115–120 °C) which is attributed to the presence of HDPE-like hard segments. However, the observation of a high melting point alone is not sufficient to confirm a polymer's blocky nature. When compared to random copolymers, OBCs in the solid-state have a unique crystal morphology and show improved physical properties such as compression set, elastic recovery, and abrasion resistance.[3,5]

Figure 3 shows the analytical TREF profile comparing an olefin block copolymer (0.878 g/cc, 1.5 I_2) to a random copolymer (AFFINITY^{TM} VP8770, 0.887 g/cc, 0.9 I_2) and a polymer blend (0.89 g/cc, 1.0 I_2) with components that are representative of the hard and soft segments within the olefin block copolymer. Although not a perfect comparison, the differences shown in Figure 3 cannot be reconciled by the slight differences in density and melt index of these polymers. Table 2 summarizes the analytical characteristics of these polymers. Figure 3 shows that for this particular OBC, 90 wt% of the polymer eluted at a peak temperature of 80 °C. The nearly complete elution of this OBC, despite being 0.878 g/cc (19 wt% crystallinity) is unique when compared to the blend and random copolymer that have peak elution percentages of 35 wt% and 75 wt%, respectively. For the 0.889 g/cc blend, the 35 weight % of the ATREF peak is consistent with the targeted amount of high crystallinity polymer made. The fraction eluting below 30 °C

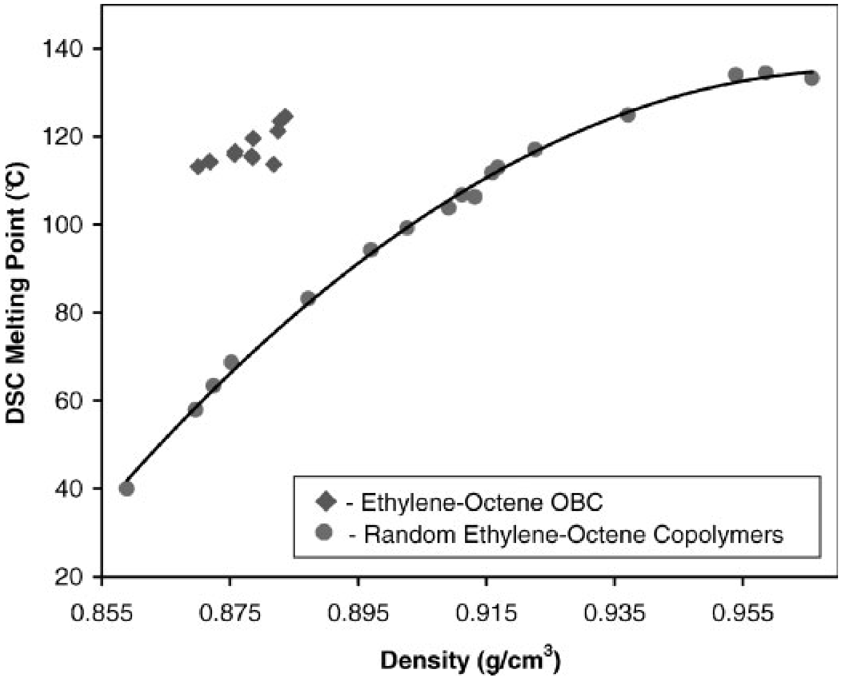


Figure 2.
Melting point characteristic of olefin block copolymers.

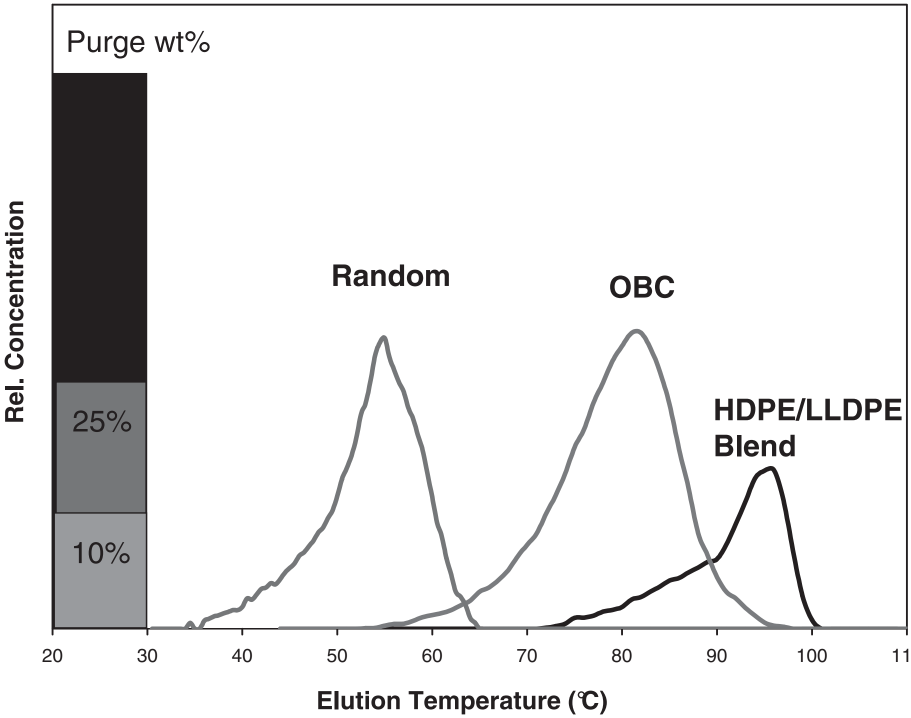


Figure 3.
Analytical TREF profile of an OBC, a random copolymer, and a polymer blend.

is referred to as the non-crystalline or ‘‘purge’’ fraction and contains the soft, low crystallinity polymer made. The 55 °C elution temperature and 75 weight percent peak area for the VP8770, random copolymer is consistent with its 0.887 g/cc density and 0.9 I_2. For the OBC, the area of the eluted peak was significantly higher than the targeted amount of hard segments in the overall polymer (29 wt% hard segments for this particular OBC). This indicates that the hard segments dominate the elution behavior of the OBC and are present in the backbone of the chains (supporting the contention that the soft, lower crystallinity segments are connected to the hard, higher crystallinity segments, which provides an indication of its blocky nature).

To confirm this observation, preparative TREF fractionation was carried out. Fractions were eluted in 5 °C increments and then analyzed for their octene content by NMR. Figure 4 and Tables 3–4 shows the expected behavior of the fractions prepared from an LLDPE produced by Ziegler-Natta catalysis (ATTANE™ 4203, 0.90 g/cm^3, 0.8 I_2) and an LLDPE produced by

Table 2.
Analytical characteristics of the polymers studied.

Example	Density (g/cc)	Mol % Octene	I2	I10/I2	M_w	M_w/M_n	Heat of Fusion	Crystallinity	T_m	T_c	ATREF Elution T	wt% Peak
	(g/cc)	(mol %)			(g/mol)		(J/g)	Wt%	(°C)	(°C)	(°C)	wt%
Random (VP8770)	0.8872	9.1	0.9	8.2	98000	2.2	74.8	25.6	83.2	65.1	55	75
Blend	0.8895	9.3	0.9	13.4	137300	13.8	90	30.8	125	111	82	35
OBC	0.8786	10.8	1.5	6.7	104600	2.0	55	18.8	120	101	96	90

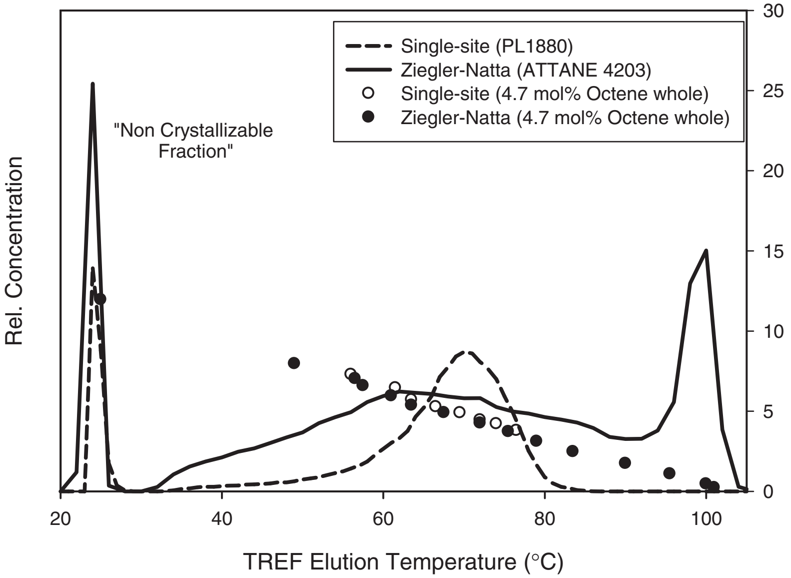


Figure 4.
Comonomer versus elution temperature relationship for random copolymers.

single-site catalysis (AFFINITY™ PL1880, 0.90 g/cm^3, 1 I_2). As shown for these polymers produced with the same comonomer type, a distinct relationship between the elution temperature and comonomer content is observed, indicating that regardless of the catalyst nature, the fractions from these random copolymers, for all practical purposes, have a statistically random distribution of comonomer. Wild has demonstrated that the peak elution temperature directly relates to the degree of short chain branching in a copolymer.[6] Brull et al. has demonstrated that the melting point or crystallization point depression of propylene-alpha olefin copolymers occurs linearly with increasing comonomer content and type regardless whether the analysis was performed in the melt or solution.[7]

Table 3.
Ziegler-Natta LLDPE TREF fractionation results.

Example - Ziegler-Natta Ethylene-Octene Copolymer (ATTANE™ 4203, 0.90 g/cc, 0.8 I2)

Fractionation Temperature (°C)	Weight Fraction Recovered	ATREF T (°C)	Mol % Octene (NMR)
20	0.08	20	12.0
20–35	0.02	46.5	10.0
35–40	0.050	49	8.0
40–45	0.035	56.5	7.0
45–50	0.047	57.5	6.6
50–55	0.067	61	6.0
55–60	0.079	63.5	5.4
60–65	0.105	67.5	4.9
65–70	0.104	72	4.3
70–75	0.110	75.5	3.7
75–80	0.089	79	3.1
80–85	0.062	83.5	2.5
85–90	0.045	90	1.7
90–95	0.041	95.5	1.1
95–100	0.056	100	0.5
100–105	0.007	101	0.2

Table 4.
Single-site LLDPE TREF fractionation results.

Example – Single-site Ethylene-Octene Copolymer (AFFINITY™ PL1880, 0.90 g/cc, 1.0 I2)

Fractionation Temperature (°C)	Weight Fraction Recovered	ATREF T (°C)	Mol % Octene (NMR)
40–45	0.025	56	7.3
45–50	0.041	61.5	6.5
50–55	0.073	63.5	5.7
55–60	0.124	66.5	5.3
60–65	0.180	69.5	4.9
65–70	0.228	72	4.4
70–75	0.241	74	4.2
75–80	0.050	76.5	3.8

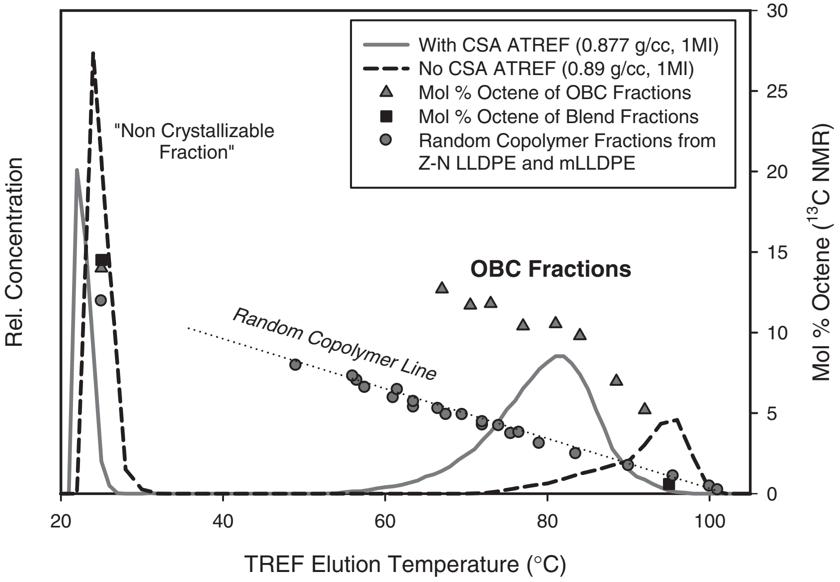


Figure 5.
Comonomer versus elution temperature of OBC.

Figure 5 and Tables 5–6 show the results for the OBC and in-reactor blend. Strikingly, it can be seen that for a given ATREF elution temperature, the octene content of the preparative fractions from the OBC copolymer is significantly higher than that of the preparative fractions from traditional random copolymers.

The expected comonomer composition versus elution temperature is shown by the calibration line for random copolymers. In terms of the distribution of comonomer in this OBC, it can be concluded that the comonomer distribution is statistically nonrandom and highly blocked (or segmented). Thus, for the high elution temperatures observed, the comonomer content of the fractions is significantly higher due to the presence of the octene-rich soft segment within the chain. In comparison, the octene content of the fraction from the in-reactor blend produced with no chain shuttling agent falls along the random copolymer line as expected.

Table 5.
OBC TREF fractionation results.

OBC TREF Fractionation (0.8786 g/cc, 1.5 I2)			
Fractionation Temperature (°C)	Weight Fraction Recovered	ATREF T (°C)	Mol % Octene (NMR)
20	0.162	20	14.1
20–60	0.104	67	13.7
60–65	0.040	70.5	12.6
65–70	0.053	73	12.2
70–75	0.126	77	11.7
75–80	0.220	81	10.5
80–85	0.192	84	9.8
85–90	0.065	88.5	7.0
90–95	0.019	92	5.2

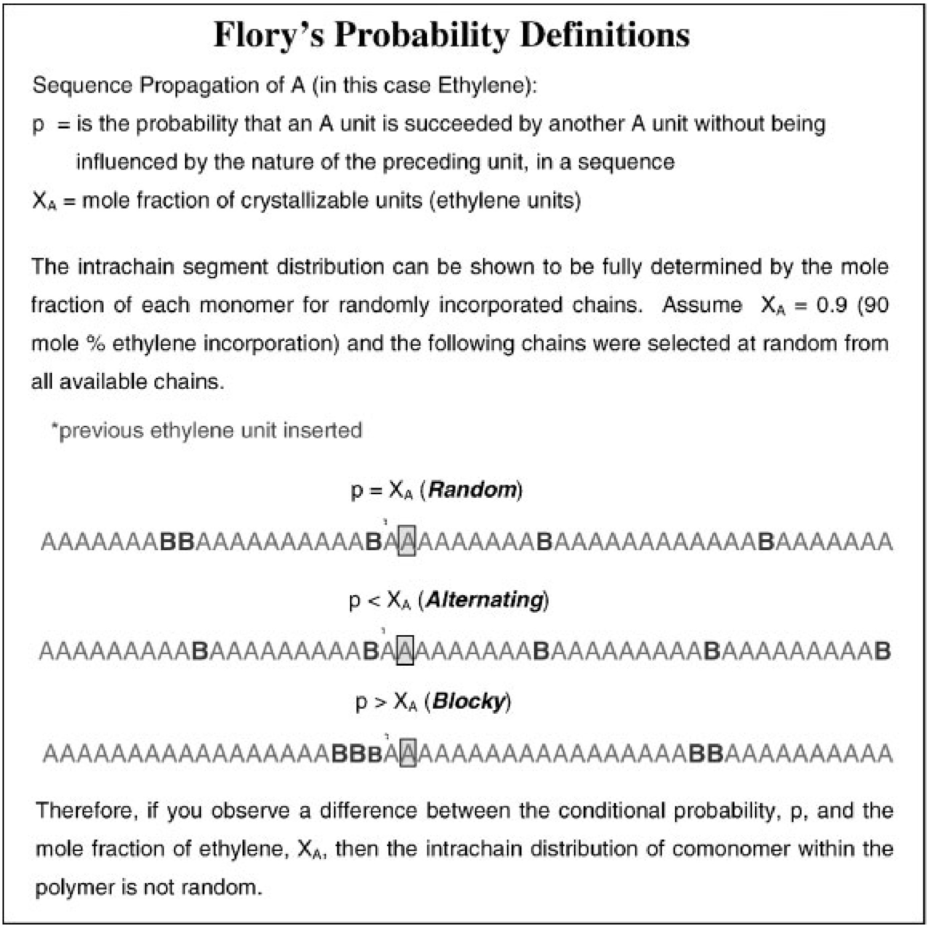
Random Versus Block Copolymers

The observation that the TREF fractions from an OBC contain a higher than expected amount of comonomer demonstrates that the intrachain comonomer distribution or sequence distribution is

Table 6.
In-reactor blend TREF fractionation results.

BLEND TREF Fractionation (0.8895 g/cc, 0.9 I2)			
Fractionation Temperature (°C)	Weight Fraction recovered	ATREF T (°C)	Mol % Octene (NMR)
20	0.63	20	14.5
20–105	0.37	96	0.6

non-random and is in fact blocked, because it deviates from that of a statistically random copolymer in a theoretically predictable manner. Since the amount of comonomer can be predicted from a given elution temperature for a statistically random copolymer, the ‘‘blockiness’’ of an olefin block copolymer can be defined on the basis of Flory's equilibrium crystallization theory.[8] For random copolymers, Flory proposed a theoretical relationship for the probability of having a minimum crystallizable sequence length determined primarily by the equilibrium crystallization temperature. The conditional probability of sequential monomer insertion (ethylene in the case of the OBCs described here) is defined as p. The magnitude of the conditional probability, p, is compared to the molar fraction of monomer in the whole polymer, X_A, (refer to Figure 6) to test whether, based on a random probability of the intrachain monomer distribution, the copolymer is random. If the conditional probability of observing a crystallizable sequence is less than that determined by average molar monomer content of the whole polymer, then the polymer is described as having an alternating distribution. If the probability of observing a crystallizable sequence was greater than that determined by the average molar monomer content of the whole polymer, then the polymer is described as having a blocky



Flory's Probability Definitions

Sequence Propagation of A (in this case Ethylene):

p = is the probability that an A unit is succeeded by another A unit without being influenced by the nature of the preceding unit, in a sequence

X_A = mole fraction of crystallizable units (ethylene units)

The intrachain segment distribution can be shown to be fully determined by the mole fraction of each monomer for randomly incorporated chains. Assume $X_A = 0.9$ (90 mole % ethylene incorporation) and the following chains were selected at random from all available chains.

*previous ethylene unit inserted

$p = X_A$ (***Random***)

AAAAAAA**BB**AAAAAAAAAA**B**$\overset{*}{\text{A}}\boxed{\text{A}}$AAAAAAA**B**AAAAAAAAAAAA**B**AAAAAAA

$p < X_A$ (***Alternating***)

AAAAAAAAA**B**AAAAAAAAA**B**$\overset{*}{\text{A}}\boxed{\text{A}}$AAAAAAA**B**AAAAAAAAA**B**AAAAAAAAA**B**

$p > X_A$ (***Blocky***)

AAAAAAAAAAAAAAAAA**BBB**$\overset{*}{\text{A}}\boxed{\text{A}}$AAAAAAAAAAAAAAAA**BB**AAAAAAAAAA

Therefore, if you observe a difference between the conditional probability, p, and the mole fraction of ethylene, X_A, then the intrachain distribution of comonomer within the polymer is not random.

Figure 6.
Flory's polymer probability definitions.

structure. Finally, if the conditional probability and molar fraction are equal, the copolymer is random.

In the discussion below, we chose to express the mole fraction of ethylene as P, with the understanding that it is only equivalent to the conditional probability, p, described above when the copolymer is random. From this point forward, we will consider the measured mole fraction of ethylene (X) from NMR or other technique for a polymer as an estimate of the conditional probability.

Having now proposed a "blocky" structure for the OBC, we are in a position to validate the proposed structure on the basis of Flory's equilibrium melting theory as extended to the ATREF elution temperature. The key relationship of Flory's theory is:[8]

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\left(\frac{R}{\Delta H_u}\right) \ln P \qquad (1)$$

In Equation (1) the mole fraction of crystallizable monomers, P, is related to the melting temperature, T_m, of the copolymer, and the melting temperature of the pure crystallizable homopolymer, T_m^0. The equation is similar to the experimentally determined relationship for the natural logarithm of the mole fraction of ethylene as a function of the reciprocal of the ATREF elution temperature or melting point (°K) as shown in Figure 7 for various homogeneously branched copolymers of ethylene. *Note: The ATREF Elution Temperature-NMR calibration depicted in* Figure 7 *is not intended to be "universal" in that ATREF instrumentation and methodology varies considerably in the literature. The calibration in this paper is therefore to be considered to be unique and must be repeated for each ATREF instrument. Also, the preparative TREF fractions or homogeneous random copolymers that were chosen have weight average molecular weights of at least 100,000 daltons and polydispersity values of no greater than about 2.5.*

Preparative TREF fractions of nearly all random copolymers and their blends fall on this line, except for the small, predictable effects of molecular weight. According to Flory's definition, if one observes a difference between the measured (X) and predicted value (P) of the mole fraction of

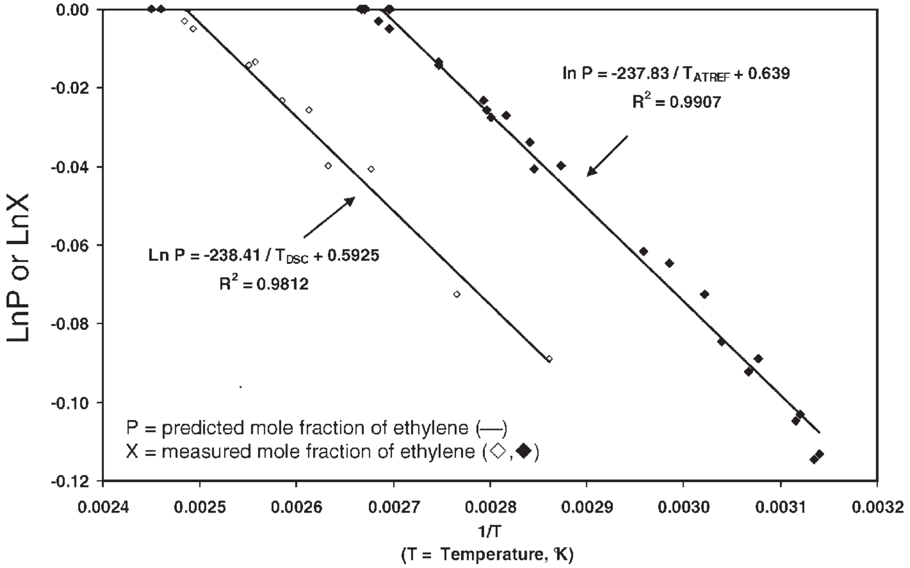


Figure 7.
The relationship of ethylene mole fraction to ATREF peak elution temperature (◆) and DSC melting temperature (◇) for various homogeneously branched copolymers can be interpreted on the basis of Flory's equation.

ethylene in an unknown polymer, then the intrachain distribution of comonomer within the polymer is not random.

A TREF fraction of a blocky copolymer should have more comonomer (octene) than a comparable random copolymer fraction with the same ATREF elution temperature (or DSC melting temperature). Figure 8 shows that TREF fractions from the OBC all lie below the random copolymer line when plotted as ln X versus $1/T_{\mathrm{ATREF}}$. Thus, they have more octene than their random counterparts at the same TREF elution temperature.

Block Index

The mole fraction of ethylene in random copolymers is determined by the underlying statistic(s) of the ethylene segment distribution produced during the polymerization. The crystallization behavior, and ultimately the minimum equilibrium crystal thickness at a given crystallization temperature and melting temperature provides a useful way to at least qualitatively measure how "blocky" a given TREF fraction is relative to its random equivalent copolymer (or random equivalent TREF fraction). In Figure 8, the ln X versus $1/T_{\mathrm{ATREF}}$ relationship shows the magnitude of the deviation of an OBC fraction from the expected random relationship. However, it is important to realize that there are two random equivalents for a given blocky fraction, one corresponding to constant elution or melting temperature and one corresponding to constant mole fraction of ethylene. These form the sides of a right triangle as shown in the Figure 9.

For any of the fractions in Figure 9, the distance to the random copolymer line is easily calculated using Pythagorean Theorem with the guidance of Figure 9.

In Figure 9, the T_X and X_X values are the ATREF elution temperature and the ethylene mole fraction measured by NMR, respectively, for an arbitrary preparative TREF fraction from an olefin block copolymer. The T_A and P_A values are the ATREF elution temperature and the ethylene mole fraction for the pure "hard segment". This point can be set to values for high density polyethylene homopolymer or it can be set to values corresponding to the actual hard segment, if known. The P_{AB} value corresponds to the measured (NMR) ethylene mole fraction in the whole polymer prior to fractionation and the T_{AB} value corresponds

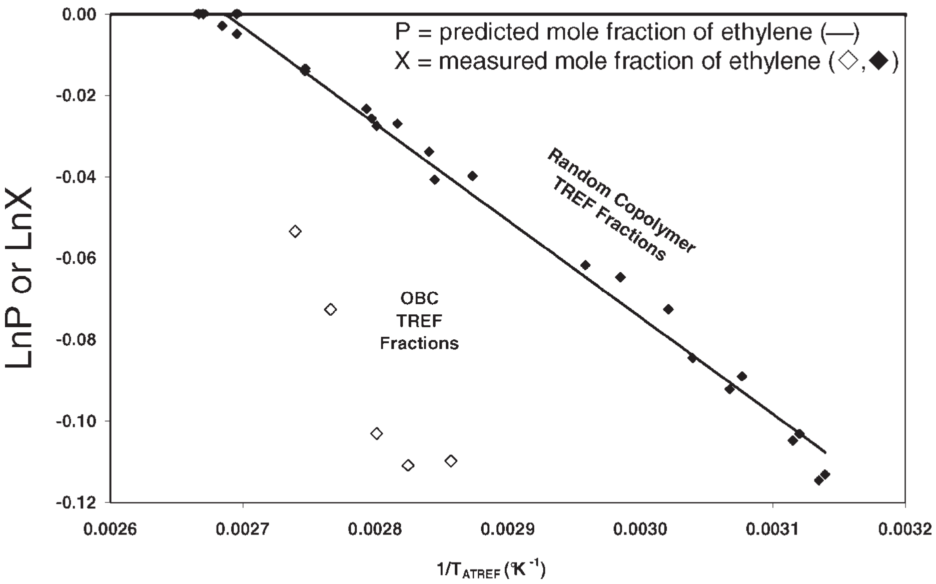


Figure 8.

OBC TREF Fractions (◇) have higher comonomer content than random equivalents (◆).

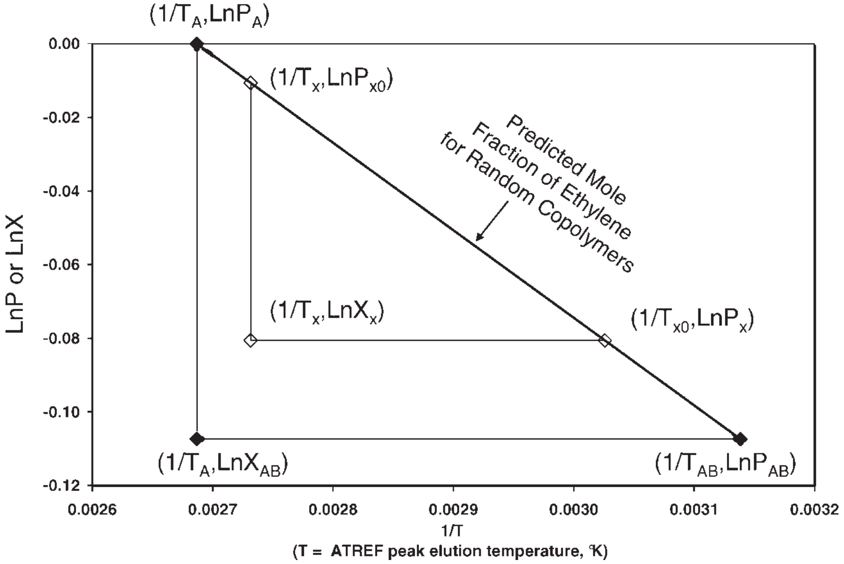


Figure 9.
Graphical definitions for the "Block Index" methodology.

to the calculated random copolymer equivalent ATREF elution temperature based on the measured P_{AB}. From the measured ATREF elution temperature, T_X, the corresponding random ethylene mole fraction, P_{X0}, can also be calculated. Similarly, from the measured NMR composition, X_X, the corresponding random elution temperature, T_{X0}, can be calculated. The square of the block index (BI) is defined to be the ratio of the area of the ($T_{X,}$ X_x) triangle and the (T_A, X_{AB}) triangle, as described in Equations (2) and (3). Since the right triangles are similar, the ratio of areas is also the squared ratio of the distances from (T_A, X_{AB}) and (T_X, X_X) to the random line. In addition, the similarity of the right triangles means the ratio of the lengths of either of the corresponding sides can be used instead of the areas.

$$\text{Block Index} = \frac{1/T_x - 1/T_{x0}}{1/T_A - 1/T_{AB}} \qquad (2)$$

$$\text{Block Index} = \frac{LnX_x - LnP_{x0}}{LnP_{AB} - LnP_A} \qquad (3)$$

The application of this calculation to TREF fractions from the OBC is shown in Figure 10 and Tables 7–8. As shown previously, the TREF fractions from the OBC lie well below the line established for random copolymers on the ln P versus $1/T_{\text{ATREF}}$ plot in Figure 8. Using the definition for T_A hard segment temperature which was set to 372.15°K (99 °C) and the linear regression parameters for the random calibration line (Table 7), the block indices were computed from the fraction's ATREF elution temperature, and molar fraction of ethylene measured from NMR. As shown, the BI values range from 0.36 to 0.69, where a higher BI value indicates a greater deviation from the expected random behavior. In contrast, for the TREF fraction from the blend which had an ATREF elution temperature of 96 °C and 0.6 mol% octene, the calculated BI value was zero; thus indicating that the fraction is random in nature. This last result was expected since no chain shuttling agent was used to make this polymer.

Now that the method to calculate the BI value has been established, to further quantify these parameters, an average BI and BI breadth can be calculated using the amount of polymer recovered for each

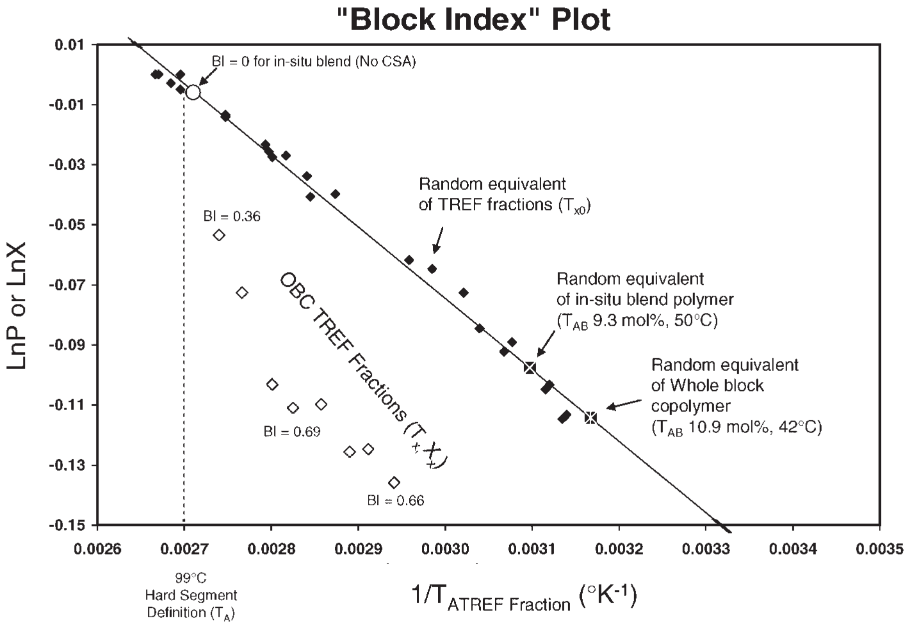


Figure 10.
Block Index results for TREF fractions of an OBC.

fraction. This provides a weighted average of the block index and can be used as a value to quantify the overall deviation of the whole polymer from the expected random behavior, as shown in Equation (4). Additionally, by calculating the second moment about the mean, a breadth index can be developed that relates to the uniformity of the block indices observed, see Equation (5).

$$\text{Average BI} = \overline{BI} = \sum (w_i \cdot BI_i) \tag{4}$$

$$\text{BI Breadth} = \sqrt{\frac{\sum w_i (BI_i - \overline{BI})^2}{\frac{(N-1)\sum w_i}{N}}} \tag{5}$$

Table 8 shows the complete calculation for the OBC example. The average block index (ABI) for this OBC is estimated to be 0.531 and the block index breadth is 0.136. Table 9 shows the block index results for the in-reactor blend (produced with no CSA) and the Ziegler-Natta LLDPE and single-site LLDPE. As expected, the block index average is reported to be zero for these polymers.

Further Applications of the Block Index

As demonstrated above, the method can be used to quantify the deviation of olefin block copolymers with a crystallizable hard

Table 7.
Preliminary values needed for block index calculations.

Variable Name	Value	Explanation
tSlope	−237.8341	Slope of regression line for Log_e of the mole fraction of ethylene versus reciprocal of analytical TREF elution temperature (°K)
tIntc	0.6390	Intercept of regression line for Log_e of the mole fraction of ethylene versus reciprocal of analytical TREF elution temperature (°K)
T_A	372.15	Analytical TREF elution temperature (°K) of hard segment
P_A	1.000	Mole fraction of ethylene of hard segment
P_{AB}	0.892	Mole fraction of ethylene in whole polymer
T_{AB}	315.722	Equivalent analytical TREF elution temperature (°K) of whole polymer calculated from whole polymer ethylene content

Table 8.
Fractionation Block Index (BI) calculations.

Fraction #	Weight Recovered (g)	ATREF Elution Tempera–ture (°K)	Mole Fraction Ethylene (NMR)	Weight Fraction Recovered	Random Equivalent ATREF Tempera-ture from NMR Ethylene Weight Fraction (°K)	Random Equivalent mole fraction ethylene from ATREF Tempera-ture	Fractional Block Index based on Tempera-ture formula	Fractional Block Index based on Log_e of mole fraction formula	Weighted Fractional Block Indices	Weighted Squared Deviations about the Weighted Mean
	Array Variable Name->	T_x	X_x	w	T_{Xo}	P_{Xo}	fBI	fBI	w * fBI	w * (fBI - ABI)
1	3.0402	(Note 1)	0.859	0.165	(Note 1)	(Note 1)	0	0	0	(Note 1)
2	1.9435	340	0.873	0.106	307	0.941	0.659	0.659	0.070	0.0017
3	0.7455	343.5	0.883	0.041	312	0.948	0.622	0.622	0.025	0.0003
4	1.0018	346	0.882	0.054	311	0.953	0.676	0.676	0.037	0.0011
5	2.3641	350	0.896	0.128	318	0.960	0.607	0.607	0.078	0.0007
6	4.1382	354	0.895	0.225	317	0.968	0.684	0.684	0.154	0.0052
7	3.5981	357	0.902	0.195	320	0.973	0.665	0.665	0.130	0.0035
8	1.2280	361.5	0.930	0.067	334	0.981	0.470	0.470	0.031	0.0003
9	0.3639	365	0.948	0.020	343	0.987	0.357	0.357	0.007	0.0006
Totals:	18.4233	Total Weight		1.000	Normalization check		Weighted Sums		0.531	0.0135

Final Calculations

Weighted Average Block Index (ABI)	0.531
Partial sum of weights with fBI > 0 (See Note 2 above)	0.835
Square root of sum of weighted squared deviations about the weighted mean	0.136

Note 1: Fraction #1 does not crystallize in the analytical ATREF and is assigned fBI = 0.

Note 2: The weighted squared deviations about the weighted mean use only fBI >0.

block or segment from the expected comonomer content versus elution temperature relationship for statistically random copolymers. The most perfect block distribution (ABI equal to unity) would correspond to a whole polymer with a single eluting fraction at the point (T_A, P_{AB}). A polymer that elutes at this point would preserve the ethylene segment distribution in the ‘‘hard segment’’, yet contain all the available comonomer (presumably in runs that are nearly identical to those produced by the soft segment catalyst). In most cases the ‘‘soft segment’’ will not crystallize in the ATREF (or preparative TREF). For the examples shown, the average block index was calculated for the crystallizable polymer that elutes. To include the non-crystallizing polymer contained in the purge peak (<30 °C), block index Equation (2) and (3) can still be applied. However special consideration is required to obtain lower temperature resolution or extend the calibration using DSC measurements of the purge fraction. In the case where more resolution is required, it is possible to extend the comonomer versus temperature calibration to lower temperatures by operating the ATREF to subambient conditions using a solvent such as ortho-dichlorobenzene.

Overall, the proposed ‘‘Block Index’’ methodology is useful to quantify the deviation of an olefin block copolymer from a polymer’s expected monomer composition versus the ATREF elution temperature. If differences are observed from this relationship, it can be concluded that the intrachain distribution of comonomer

Table 9.
Block Index summary of OBC and random copolymers.

Example	Type	Chain Shuttling Agent?	Average Block Index	BI Breadth
In-reactor Blend	Blend	No CSA	0	0
OBC	Chain Shuttling	CSA	0.531	0.136
Random References				
ATTANE 4203	Ziegler-Natta	NA	0	–
AFFINITY PL1880	Single-site	NA	0	–

within the polymer is not random and that the blocks or segments within the polymer are blocked. Block indices can have a range of values between zero and unity, with unity being the largest possible deviation from random based on the hard block composition.

Conclusions

A unique structural feature of olefin based block copolymers is that the intra-chain distribution of comonomer is segmented (statistically non-random). Fractionating an olefin block copolymer by preparative temperature rising elution fractionation, TREF, results in fractions that have much higher comonomer content than comparable fractions of a random copolymer collected at an equivalent TREF elution temperature.

We have developed a "block index" methodology which quantifies the deviation from the expected monomer composition versus the analytical temperature rising elution fractionation, ATREF, elution temperature. When interpreted properly, this index indicates the degree to which the intra-chain comonomer distribution is segmented or blocked. The unique crystallization behavior of block copolymers determine the magnitude of the block index values because the highly crystalline segments along an otherwise non-crystalline chain tend to dominate the ATREF (and DSC) temperature distributions.

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