

# Influence of the Short-Chain Branch Length on the Calibration of Temperature Rising Elution Fractionation Systems

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**ABSTRACT:** The effects of short-chain branch (SCB) length on the calibration of temperature rising elution fractionation (TREF) were examined. Samples of ethylene–hexene, ethylene–octene, and a novel polyolefin produced using Eastman Chemical Company’s Gavilan catalyst technology were used to prepare TREF calibration curves. Preparative TREF was used to collect fractions of the materials based on their crystallizability, and the branching frequencies of the fractions were determined by NMR. Calibration curves were generated by plotting the branching frequency as a function of the TREF elution temperature. The results indicate that the calibration curves shift to lower TREF elution temperatures as the length of the SCB increases from methyl to butyl to hexyl. Other factors that may contribute to this shift include chain microstructural differ-

ences from variations in catalyst structure and process conditions. The shift can be decreased by plotting the data in “number of branches per 1000 backbone carbons” versus TREF elution temperature instead of the more traditional “number of branches per 1000 total carbons.” These data indicate that the branch type must be known *a priori* to calculate SCB averages and SCB distributions and that unique calibration curves exist for copolymers made using different  $\alpha$ -olefin comonomers. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 722–728, 2003

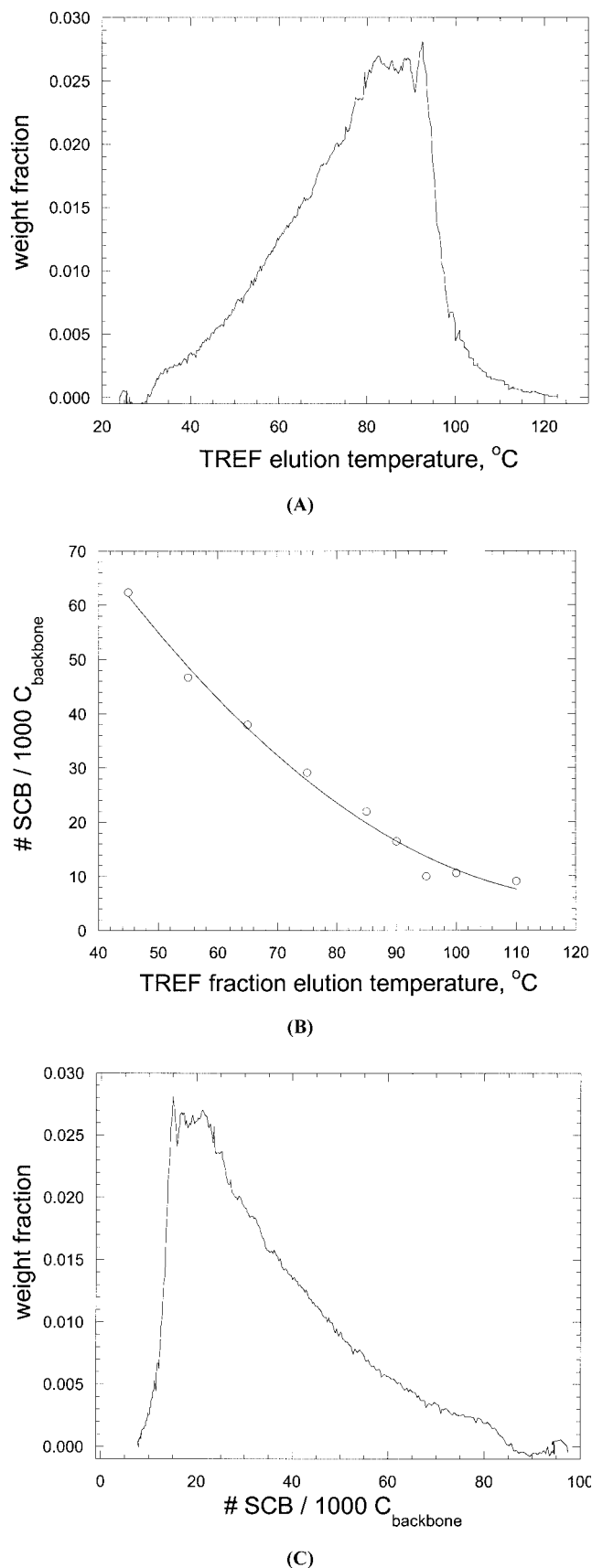
**Key words:** temperature rising elution fractionation (TREF); chain; branch distribution; short-chain branch; microstructure

## INTRODUCTION

Temperature rising elution fractionation (TREF), which separates polymer molecules according to differences in crystallizability, is the primary technique used for the analysis of short-chain branch distribution in polyolefins.<sup>1–8</sup> The experimental procedure involves melting/dissolving the polymer in a high boiling solvent and then precipitating it onto an inert support material by slowly lowering the temperature of the solution. The resulting deposit has the least crystallizable, and thus lowest melting, material at the surface, and the most crystalline, highest melting material at the core. The sample is analyzed by applying a rising temperature gradient, under solvent flow, which melts/dissolves the polymer in the reverse order in which it was deposited. Thus, the most highly branched and therefore least crystalline material is dissolved first, followed by the next most highly branched material, until finally nearly linear polymer at the core of the crystals is dissolved. The concentra-

tion of material is monitored as a function of the temperature to yield a plot such as that shown in Figure 1(a). These data are useful for qualitative comparisons, but for more detailed analyses the temperature axis is usually converted to units of short-chain branch (SCB) frequency through the use of a calibration curve such as that depicted in Figure 1(b). Although the online determination of branching frequency has been described,<sup>9</sup> such calibration curves usually result from larger-scale preparative TREF analyses where fractions having varying SCB frequencies are physically collected and isolated. These fractions are then analyzed spectroscopically, typically by NMR or IR spectroscopy, to provide a measure of the SCB frequency. By using the calibration curve, the data in Figure 1(a) can be converted to a somewhat more meaningful presentation, as shown in Figure 1(c). The data in Figure 1(c) can be used to calculate the number- and weight-average SCB averages and the short-chain branch distribution (SCBD) analogous to molecular weight averages and distribution. Although several schemes have been proposed for the development of a universal calibration curve,<sup>2,10</sup> the existence of such curves is now widely discounted. One of the factors assumed to affect the calibration is

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**Figure 1** Development of short-chain branch distribution from analytical TREF data: (a) Analytical TREF data; (b) TREF calibration curve; (c) short-chain branch distribution.

branch length. Although it has been demonstrated that branch length does affect the melting point and density of bulk samples<sup>11</sup> with the same average SCB, no studies have directly examined the effect for fractions from TREF.

This work explores the effects of branch length on the TREF calibration curve through examination of copolymers of ethylene with 1-octene and 1-hexene to give linear low-density polyethylenes (LLDPE) having hexyl and butyl branches, respectively. Also examined is a material having predominantly methyl branches that was produced from ethylene monomer alone using Eastman Chemical Company's trademarked Gavilan catalyst technology.

## EXPERIMENTAL

### Materials

The polymers chosen for this study included two LLDPEs and a novel branched polyolefin. The first LLDPE sample was Dow Chemical Company's Dowlex 3347, which is an ethylene–octene (EO) copolymer and is produced using solution-phase Ziegler–Natta technology. The second LLDPE was an Eastman Chemical Company experimental ethylene–hexene (EH) copolymer produced using gas-phase Ziegler–Natta technology. The third sample was a novel branched polyethylene made using a silica-supported version of Eastman Chemical Company's Gavilan catalyst technology that produces branched polyethylene from ethylene monomer alone.<sup>12–15</sup> The results of analysis of the bulk samples are listed in Table I.

### Gel permeation chromatography–viscometry (GPCV)

Molecular weight data for the samples were determined using a Polymer Labs (PL; Amherst, MA) 210 GPC system with 1,2,4-trichlorobenzene (TCB, 348-4; Burdick and Jackson, Muskegon, MI) as the solvent. The TCB for the analyses and sample preparation contained approximately 0.5 g of 2,6-di-*tert*-butyl-4-methylphenol (D4, 740-4; Aldrich, Milwaukee, WI) per 1000 mL of TCB as an antioxidant.

GPC samples were prepared by dissolving approximately 2.5 mg of resin in about 2 mL of TCB. The samples were dissolved at 160°C for 4 h in a heater/stirrer, and were filtered before analysis using glass wool-stuffed pipettes that were positioned in an aluminum block maintained at 160°C.

The GPC columns and detectors were maintained at 160°C. The GPC detectors were a Viscotek (Houston, TX) 210R viscometer and PL refractive index detector. The injection loop was 200  $\mu$ L and the flow rate was 1.0 mL/min. The column set consisted of three PL PLgel Mixed B 300  $\times$  7.5 mm columns and one PLgel

**TABLE I**  
Sample Physical Properties

Sample	SCB type	Bulk branching frequency (no. SCB/1000 C) <sup>a</sup>	$M_n$ (g/mol) <sup>b</sup>	$M_w$ (g/mol) <sup>b</sup>
Ethylene–octene	Hexyl	22.5	28,000	95,000
Ethylene–hexene	Butyl	25.5	17,000	82,000
Gavilan	~ 75% Methyl	26.0	63,000	230,000

<sup>a</sup> Branching data determined using <sup>1</sup>H-NMR spectroscopy.

<sup>b</sup> Molecular weight data determined using gel permeation chromatography–viscometry.

Mixed B 50 × 7.5 mm column. The system was calibrated using PL narrow molecular weight distribution polystyrenes ranging from 7000 to 7.5 million g/mol. Molecular weight calculations were performed by Viscotek TriSEC GPC software using the universal calibration procedure. Mark–Houwink–Sakurada parameters obtained from the polystyrene standards, and for each of the unfractionated polyolefin samples, are shown in Table II. Within the uncertainty of the measurements, the relationships described by the three sets of values for the polyolefins are not significantly different.

### Analytical TREF

The analytical TREF was performed using a Polymics CAP TREF system (Polymics, State College, PA) in the same solvent as used for GPC. Samples were prepared by dissolving approximately 0.01 g of resin/mL TCB at 150°C for 4 h in a Pierce (Rockford, IL) Reacti-Therm III heater/stirrer. Chromosorb P (C 5889; Sigma, St. Louis, MO) was preheated to 150°C and was added to the solution, as the crystallization support, after the samples were dissolved. The hot samples were placed in a Despatch LAC programmable forced-air oven, preheated to 150°C, and allowed to equilibrate for 2 h. The crystallization was then performed by cooling the oven from 150 to 30°C at a cooling rate of 2°C/h. This step was determined by Polymics to be the most critical determinant of separation efficiency in TREF, and it is important that it be done at a slow rate of cooling. The subsequent dissolution may be much more rapid, given that the important parameter is not the heating rate, but rather the volume of solvent per degree of temperature rise.<sup>16</sup>

**TABLE II**  
Mark–Houwink–Sakurada Parameters for Polystyrene Calibrants and Unfractionated Polyolefins

Sample	$K \times 10^4$ (dL/g)	$\alpha$
Polystyrene	1.39	0.697
Ethylene–octene	2.85	0.751
Ethylene–hexene	1.77	0.794
Gavilan	5.51	0.703

The resulting crystallized samples were packed into the Polymics CAP TREF analytical cartridge and subjected to an analytical TREF analysis. These analyses consisted of flowing TCB at a rate of 10 mL/min at 25°C for 5 min over the sample and then ramping the temperature from 25 to 135°C at a heating rate of 200°C/h under a TCB flow rate of 20 mL/min. The concentration detector was an infrared detector set to monitor the C–H stretch region at 3.41 μm or about 2933 cm<sup>-1</sup>.

### Preparative TREF

The Polymics CAP TREF system was used in the preparative mode to collect fractions. Samples were prepared by dissolving approximately 0.015 g of resin per mL of TCB at 150°C for 4 h in a Pierce Reacti-Therm III heater/stirrer before adding Chromosorb P, preheated to 150°C, as the crystallization support. The sample size in the preparative mode was approximately 300 mL. The samples were crystallized following the same procedure given above.

Fractions were collected at 10°C intervals from 40 to 110°C, as detailed in Table III, with a solvent flow rate of 10 mL/min. The preparative TREF cartridge was held at each fraction collection temperature for 50 min before proceeding to the next fraction collection temperature at a heating rate of 100°C/h. The preparative fractionation of the Gavilan sample was modified by starting the fractionation at 45°C instead of 40°C and by collecting in 5°C increments from 85 to 100°C.

The fractions were precipitated with the addition of an excess volume of acetone while stirring. After cooling to room temperature, the polymer was isolated by vacuum filtering using 0.5-μm Zefluor 47-mm-diameter filters (P5PQ047; Pall Gelman Sciences, East Hills, NY) and washing with additional acetone to remove residual TCB.

### <sup>1</sup>H-NMR

Polyolefin samples were prepared by dissolving 10 to 15 mg of polymer in about 1 mL of *ortho*-dichlorobenzene-D<sub>4</sub> (Cambridge Isotope Laboratories, Woburn, MA) at 130°C in a 5-mm NMR tube. Proton NMR

TABLE III  
Preparative TREF Fraction Collection Data

Fraction collection temperature for LLDPE samples (°C)	No. SCB/1000 $C_{total}$		Fraction collection temperature for Gavilan sample (°C)	No. SCB/1000 $C_{total}$ Gavilan
	EH	EO		
40	49.9	36.7	45	58.7
50	35.2	26.9	55	44.6
60	34.8	22.3	65	36.6
70	22.2	17.4	75	28.3
80	16.5	12.2	85	21.5
90	8.7	7.6	90	16.2
100	10.3	2.1	95	9.9
110	3.0	1.0	100	10.5
			110	9.0

spectra were taken on a JEOL (Peabody, MA) 400-MHz spectrometer with the sample temperature set at 130°C. Typically, 256 scans were taken using a 15-s pulse delay between each scan.

The branch frequency was calculated by comparison of peak areas representing methyl, methylene, and methine protons to determine the ratio of methyl end groups to the total number of carbons. It was assumed that the backbone of each polymer molecule had a methyl group at one end and either a terminal or an internal double bond at the other. When molecular weights were low enough to detect the unsaturation, a correction was applied to the data to account for the backbone ends. Before calculation of branching frequency, the intensity of the methyl peak was reduced by an amount equal to one methyl group per observed double bond. In most cases this correction was small, a reduction of one or fewer branches per 1000 carbons.

## RESULTS AND DISCUSSION

Analytical TREF curves for the three starting materials are shown in Figure 2. From these data it can be seen that all three materials have broad SCBD and contain a variety of chains, from those that are highly branched and low melting to those that are sparsely branched and have high melting temperatures. Preparative TREF was then performed on the same samples, and calibration curves were constructed by plotting the highest TREF elution temperature for that fraction against the SCB frequency of that fraction as determined by  $^1\text{H-NMR}$ .

Branching frequency has most commonly been reported as the number of SCB/1000 total carbons, and the calibration data in Figure 3 are presented in this way. The uncertainty in the determination of branch frequency for each fraction is of the order of plus or minus one branch per 1000 carbons, or about the size of the plotted symbols. In agreement with the earlier work on bulk samples,<sup>11</sup> the data indicate that, for a given branch frequency, the TREF elution temperature

shifts to lower values as the branch length increases, methyl to butyl to hexyl. Therefore, as the length of the branch increases, the branches become more effective at disruption of regular packing and thus decrease the melting point of the crystalline regions.

The presentation of SCB frequency as the number of branches per total carbons does not take into account the increasing percentage of carbons that are involved in the branches themselves as the branch length increases. If the crystallizability is determined by the linear regions between branch points, then it may be argued that a better way to compare samples of different branch length would be to express the branching frequency in terms of backbone carbons only, SCB/1000  $C_{backbone}$ . Karbasheski et al.<sup>17</sup> previously presented SCBD data in this way, calculated from monomer sequence information obtained from  $^{13}\text{C-NMR}$ , but without comment as to how or why it differed from the more common presentation.

When the length of the branches is known, the branching frequency in terms of total carbons may be

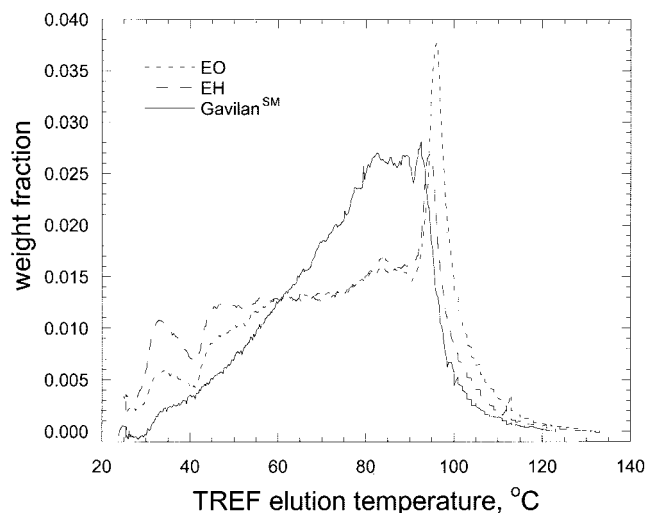
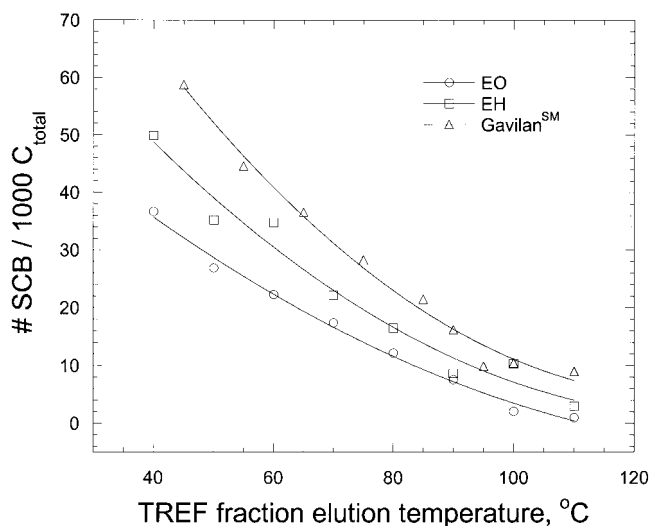


Figure 2 Analytical TREF results for bulk samples employed in the fractionation and calibration procedures.



**Figure 3** Calibration curves for ethylene–octene, ethylene–hexene, and Gavilan.

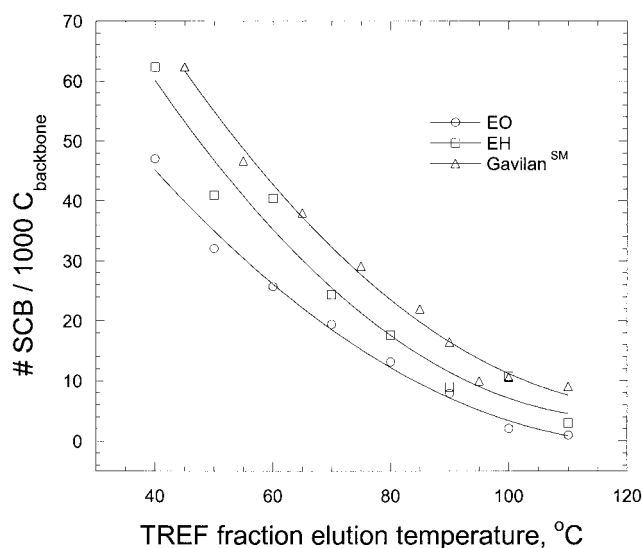
easily converted into terms of backbone carbons. The number of carbons in branches per 1000 total carbons is just the product of the number of branches per 1000 total carbons and the number of carbons in each branch. Subtraction of the resulting value from 1000 then yields the number of backbone carbons per 1000 total carbons. The branching frequency in terms of SCB per 1000 backbone carbons is found by multiplying the branch frequency per 1000 total carbons by 1000 and dividing by the number of backbone carbons per 1000 total carbons. The result is

$$F_{\text{backbone}} = 1000 \left( \frac{F_{\text{total}}}{1000 - F_{\text{total}}B} \right)$$

where  $F_{\text{backbone}}$  and  $F_{\text{total}}$  are the branching frequencies in terms of branches per 1000 backbone carbons and branches per 1000 total carbons, respectively; and  $B$  is the number of carbons per branch.

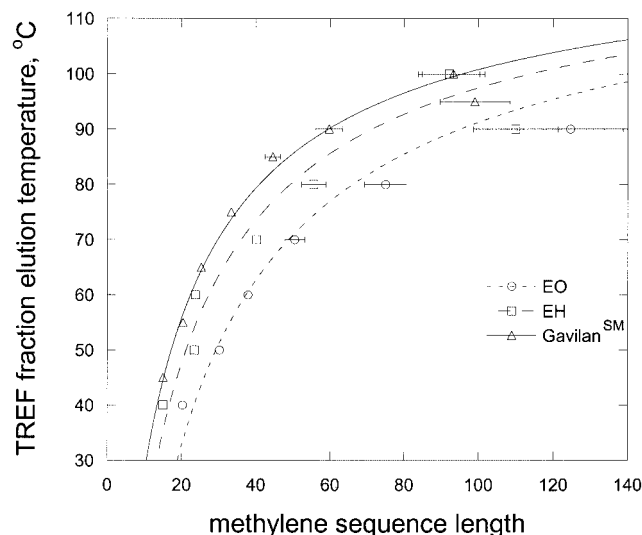
The calibration curves are presented in terms of branches per 1000 backbone carbons in Figure 4. The correction shifts the calibration curves closer together relative to the previous presentation; however, the differences among the corrected curves still result in SCB values that differ by roughly 15% from one to the next at any given dissolution temperature. These results demonstrate that the effect of the SCB length on the TREF calibration is real and not simply an artifact of the manner in which the SCB frequency is defined.

Bonner et al.<sup>10</sup> argued that the crystallizability is primarily a function of the length of the linear regions between branch points, and asserted that a universal TREF calibration results from a plot of elution temperature versus average methylene sequence length (MSL). They determined the elution volumes for several unbranched polyolefins, fitted the results to an



**Figure 4** TREF calibration curves expressed in terms of SCB/1000  $C_{\text{backbone}}$ .

equation describing the melting point of  $n$ -alkanes,<sup>18,19</sup> and applied this to analytical TREF curves for two LLDPE samples, without testing against independent determinations of SCB frequency. The present data can be used to verify the applicability of this procedure. The average MSL is calculated by dividing 1000 by the number of SCB per 1000 backbone carbons and subtracting one, for the methine carbon at the branch point. Figure 5 is a plot of the resulting values, fitted as described by the previous authors, with the temperature of last elution of polymer in each of the analytical TREF curves taken as 125°C. The data at the smallest SCB frequencies were omitted from the plot because the propagation of error in the conversion results in very large uncertainty in the respective

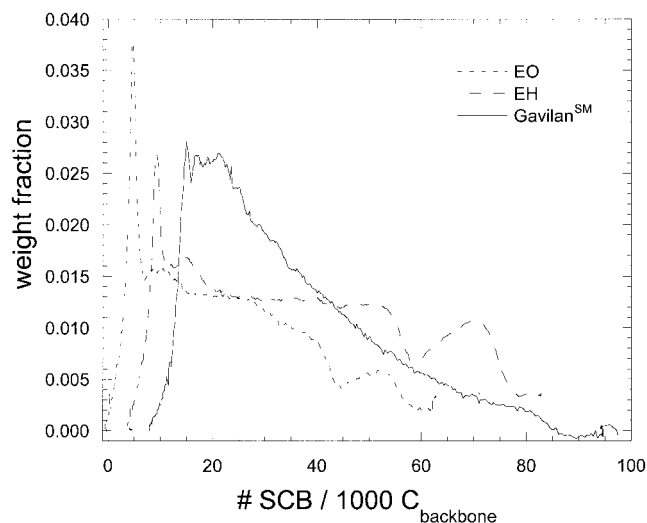


**Figure 5** Elution temperature versus average methylene sequence length.

MSL, the fit is insensitive to these points, and because it was suggested<sup>10</sup> that the relationship may not hold above MSL of 250 because of the occurrence of chain folding. It is not clear from Figure 5 whether the melting equation is appropriate for fitting the TREF results for branched polymers, although it is apparent that the data for polymers of different branch length do not follow a universal curve.

Short-chain branch distributions for the samples in this study, calculated using the respective corrected TREF calibration curves from Figure 4, are illustrated in Figure 6. From the data one can see that the EH sample has a larger proportion of nearly linear, or high-density polyethylene than the Gavilan sample and that the EO material has an even higher proportion. These differences in the high-density portion are possibly explained in the LLDPE cases by differences in the reactivity of the comonomers that should favor production of linear polyethylene as the comonomer branch length increases. These differences are apparent in the traditional analytical TREF curves, as depicted in Figure 2, but are more easily seen in Figure 6.

The number-average ( $\langle \text{SCB} \rangle_n$ ) and weight-average ( $\langle \text{SCB} \rangle_w$ ) short-chain branch values are obtained through the use of the proper TREF calibration curves. The ratio of  $\langle \text{SCB} \rangle_w / \langle \text{SCB} \rangle_n$  is used to define the breadth of the short-chain branch distributions (SCBD). Values for the  $\langle \text{SCB} \rangle_n$  and  $\langle \text{SCB} \rangle_w$  are calculated by integrating the areas under the TREF curves in a manner analogous to gel permeation chromatography data.<sup>20,21</sup> The results of applying this procedure are shown in Table IV. The SCBD values correctly capture the fact that the Gavilan sample has the narrowest SCBD, whereas the EO sample has the broadest. This can be confirmed from the data in Figures 2 and 6.



**Figure 6** TREF results expressed in terms of SCB distribution. Each curve was calculated from the corrected calibration curve specific to that polymer.

**TABLE IV**  
Short-Chain Branch Distribution Data

Sample		$\langle \text{SCB} \rangle_n$	$\langle \text{SCB} \rangle_w$	SCBD index
Ethylene–octene	Uncorrected	16.8	26.8	1.60
	Corrected	19.9	34.8	1.75
Ethylene–Hexene	Uncorrected	25.9	36.3	1.40
	Corrected	30.3	45.2	1.50
Gavilan	Uncorrected	27.3	33.8	1.24
	Corrected	28.2	35.6	1.26

## CONCLUSIONS

The data presented here demonstrate that branch length does affect the TREF crystallization and separation processes. This study indicates that, for samples with equivalent short-chain branching frequency, the TREF elution temperature decreases as the branch length increases. The effects of differing catalysts and process conditions may also have contributed to the differences seen in these experiments. Ultimately, samples having varying branch lengths, but polymerized under more similar catalyst and process conditions, would be needed to quantitatively discern the effects of the SCBs on the TREF separation process. In any event, these data imply that separate TREF calibration curves are necessary when comparing samples having different chain microstructures and that the sample SCB type should be identified before TREF analysis. Presenting the SCB frequencies in terms of backbone carbons in place of total carbons decreases the effects that branch length has on the calibration curves. However, this correction does not eliminate the necessity to create separate calibration curves for copolymers having different SCB lengths. Short-chain branch distribution values can be calculated from TREF data and used to describe differences in the dispersity of the distributions.

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