

## ANALYSIS OF BRANCHING DISTRIBUTION IN POLYETHYLENES BY DIFFERENTIAL SCANNING CALORIMETRY

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**Abstract** Short chain branching has been characterized using thermal fractionation, a stepwise isothermal crystallization technique, followed by a melting analysis scan using differential scanning calorimetry. Short chain branching distribution was also characterized by a continuous slow cooling crystallization, followed by a melting analysis scan. Four different polyethylenes were studied: Ziegler-Natta gas phase, Ziegler-Natta solution, metallocene, constrained-geometry single site catalyzed polyethylenes. The branching distribution was calculated from a calibration of branch content with melting temperature. The lamellar thickness was calculated based on the thermodynamic melting temperature of each polyethylene and the surface free energy of the crystal face. The branching distribution and lamellar thickness distribution were used to calculate weight average branch content, mean lamellar thickness, and a branch dispersity index. The results for the branch content were in good agreement with the known comonomer content of the polyethylenes. A limitation was that high branch content polyethylenes did not reach their potential crystallization at ambient temperatures. Cooling to sub-ambient was necessary to equilibrate the crystallization, but melting temperature versus branch content was not applicable after cooling to below ambient because the calibration data were not performed in this way.

**Keywords** Polyethylene, Short chain branching, Lamellar thickness, Branch distribution, Thermal fractionation, DSC

### INTRODUCTION

Ethylene copolymers are made by polymerization of ethylene with  $\alpha$ -olefins, such as 1-butene, 1-hexene or 1-octene. These polymers contain short chain branches (SCB) along the polymer backbone and exhibit broad melting ranges indicating the presence of broad lamellar thickness distributions. The properties and performance of a polymer depend on the short chain branch content and its distribution in the polymer chain. The distribution of SCB depends on the conditions used for polymerization. Ziegler-Natta (ZN) catalysis gives a broad branching distribution, particularly when the solution or slurry method is used. This method must be used for 1-octene comonomer, because of its relatively high boiling temperature. The ZN gas phase polymerization gives less highly branched molecules and is suitable for 1-butene or 1-hexene comonomers. Single site catalysts, such as metallocene and constrained geometry types, provide narrow distributions of SCB of the polymers<sup>[1]</sup>.

Polyethylenes form a chain folded crystal structure where the lamellar thickness is determined by the number of methylenes between the folds. Branch points are excluded from the crystals. When the branches consist of less than about 20 methylenes they cannot take part in crystallization, so for most short branched polyethylenes the branches are excluded from the crystals. When the branches are methyl groups then they can be accommodated in the crystals as defects, but ethyl, butyl and hexyl branches are excluded, except under very rapid quench cooling rates<sup>[2]</sup>. The analysis of the thickness of the lamella is possible when a polyethylene crystallization is limited by the SCB distribution. Another way of considering the branching distribution is the mean sequence length (MSL) of methylenes between branches. There will be a minimum MSL for a chain

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segment to join a particular lamella.

The widely used method to analyze short chain branch distribution of ethylene copolymers is temperature rising elution fractionation (TREF)<sup>[3]</sup>. Since TREF requires long fractionation times with solvent, an alternative faster and more definitive method is preferred. Thermal fractionation (TF) (segregation) as an alternative tool for qualitative SCB distribution analysis of ethylene copolymers has recently been reported<sup>[4]</sup>. Thermal fractionation can segregate molecules with intramolecular branch distributions<sup>[4, 5]</sup>, whereas TREF can only separate intermolecular branch distributions. TF provides a visual way of studying the branch distribution, whereas for analysis of the distribution it is not necessary to have segregated fractions. In the present research, a simplified new method, very slow continuous cooling, that can be used as an alternative for comonomer distribution analysis with enough accuracy and minimum time using differential scanning calorimetry (DSC) is proposed. In addition, this method can be used as an alternative method to obtain lamellar thickness distribution for some branched polyethylenes. Another DSC method for segregation of the crystals of a polymer is successive self-nucleation/annealing<sup>[6]</sup>. Other experimental methods, which have been used to determine the lamellar thickness distribution, are transmission electron microscopy<sup>[7]</sup>, small angle X-ray scattering and atomic force microscopy<sup>[8]</sup>.

DSC has previously been used to measure lamellar thickness distributions using the Thomson-Gibbs equation<sup>[9]</sup>. A constraint is that the polyethylene crystals must not rearrange during the DSC scan. In this research, the polyethylene has been cooled very slowly to ensure that the formed crystals are stable. Another limitation is that copolymers cannot reach the equilibrium melting temperature. They are restricted by the mole fraction of branches in addition to the need to use realistic crystallization temperatures. The thermodynamic melting temperature of the ethylene copolymers is the quantity applicable to copolymers that is used in the method presented.

Polyethylenes show both a molar mass distribution and a branching distribution. A two-dimensional distribution analysis can be performed by using TREF followed by size exclusion chromatography on the TREF fractions<sup>[10]</sup>. The molar mass distribution can be displayed as a curve, but it is usual to provide averages to define the distribution. Typically, the number average, weight average and polydispersity are calculated, though other higher moment averages can be obtained. This type of analysis should also be possible for the branching distribution since an analogous set of averages will completely define the SCB in any polyethylene. It is the aim of this research to provide a set of parameters that quantitatively define polyethylene branching and crystal structure.

**Table 1.** Characteristics of the ethylene copolymers

| Properties<br>VLDPE2          | C <sub>6</sub> -BPE-ZN <sub>gas</sub> <sup>a</sup> | C <sub>8</sub> -BPE-ZN <sub>soln</sub> <sup>b</sup> | C <sub>4</sub> -BPE-M <sup>c</sup> | C <sub>8</sub> -BPE-S <sup>d</sup> |
|-------------------------------|----------------------------------------------------|-----------------------------------------------------|------------------------------------|------------------------------------|
| Comonomer                     | Hexene                                             | Octene                                              | Butene                             | Octene                             |
| Catalyst type <sup>e</sup>    | ZN gas                                             | ZN soln                                             | M                                  | S                                  |
| MFI (dg min <sup>-1</sup> )   | 0.78                                               | 0.94                                                | 27.0                               | 1.0                                |
| Density (g cm <sup>-3</sup> ) | 0.935                                              | 0.920                                               | 0.901                              | 0.908                              |
| $M_w$                         |                                                    | 138,000                                             | 58,000                             | 96,700                             |
| $M_w/M_n$                     |                                                    | 4.2                                                 | 2.65                               | 2.86                               |
| Comonomer content (mol %)     | 2.3                                                | 2.7                                                 | 6.3                                | 2.4                                |
| $T_m$ (°C) <sup>f</sup>       | 121.9                                              | 110.4, 118.7, 121.9                                 | 92.7                               | 105.4                              |
| $T_c$ (°C) <sup>f</sup>       | 105.9                                              | 103.1                                               | 76.6                               | 90.3                               |

<sup>a</sup>Data were taken from chemical data sheets published by the manufacturer; <sup>b</sup>Refs. [1, 5]; <sup>c</sup>Ref. [1]; <sup>d</sup>Ref. [1]; <sup>e</sup>ZN = Ziegler-Natta catalyst, gas phase or solution; M = Metallocene; S = Single-site catalyst, constrained geometry;

<sup>f</sup>Crystallization ( $T_c$ ) and melting ( $T_m$ ) temperature were obtained at scanning rates of 10 K/min

## EXPERIMENTAL

The characteristics of the four branched polyethylenes are listed in Table 1. The copolymers were chosen to be Ziegler-Natta (ZN) or single-site metallocene (M) or constrained geometry (S) catalyzed copolymers with butene, hexene or octene comonomers. The ZN polyethylenes were represented by a gas phase (gas) and a solution (soln)

or slurry polymerized system.

A Perkin-Elmer Pyris1 DSC was used for the experiments. All samples were held in the melt at 180°C for 5 min, cooled from 180°C to 10°C and again heated to 180°C from 10°C at the rate of 10 K/min. For the slow continuous cooling experiments, the sample was first heated at 180°C for 5 min, rapidly cooled to the initial crystallization temperature for the sample ( $T_{ci}$ ) and held for 1 min. After holding, the sample was continuously cooled from  $T_{ci}$  to 25°C at the very slow cooling rate of 0.08 K/min, which is the same as the average rate for thermal fractionation and of the order of TREF rates. The  $T_{ci}$  values were 127, 122, 105 and 122°C for C<sub>6</sub>-BPE-ZN<sub>gas</sub>, C<sub>8</sub>-BPE-ZN<sub>soln</sub>, C<sub>4</sub>-BPE-M and C<sub>8</sub>-BPE-S, respectively. Thermal fractionation was performed by heating to 180°C and holding for 5 min, rapidly cooling to 124°C at 200 K/min and then holding for 50 min. The sample was again rapidly cooled by 4°C at 200 K/min then held for another 50 min, and then this step was repeated sufficient times for the sample to be cooled to about 20°C. The step intervals of 4°C and the equilibration period of 50 min were chosen after testing other combinations. If larger temperature steps are chosen, then the polymer will take a longer time to equilibrate at each temperature, because equilibration is a logarithmic process. The total time for cooling was about 22 h. Finally, both treated samples were heated from 10–150°C at a rate of 10 K/min to observe their melting behavior.

The melting temperatures ( $T_m$ ) were converted into branch composition ( $B$ ) using equations derived from the data of Hosoda<sup>[11]</sup> from TREF analyses (Eqs. 1, 2 and 3). The peak areas in the case of thermal fractionation, or partial areas in the case of continuous cooling, were converted into total amount of polymer present at each level of branching by the equations derived from the data of Hosoda<sup>[11]</sup> for crystallinity ( $\chi_c$ ) at each branch content (Eq. 4, 5 and 6). The TREF analysis was limited to lower temperatures in the ambient range, whereas the DSC could be used at sub-ambient temperatures.

$$\text{1-butene copolymers: } T_m = -1.55B + 134 \quad (1) \quad \chi_c = -0.0132B + 0.82 \quad (4)$$

$$\text{1-hexene copolymers: } T_m = -1.69B + 133 \quad (2) \quad \chi_c = -0.0134B + 0.77 \quad (5)$$

$$\text{1-octene copolymers: } T_m = -2.18B + 134 \quad (3) \quad \chi_c = -0.0251B + 0.86 \quad (6)$$

Sub-ambient temperatures were found to be necessary to convert the DSC curve into a specific heat curve since the sample baseline must be at equilibrium before starting a scan. If the sample is changing, that is still crystallizing, then the initial specific heat will deviate from the expected value and the start of the DSC curve will not be suitable for analysis. All DSC curves were converted into specific heat curves so that the curves for different samples and treatments could be quantitatively compared.

Lamellar thickness ( $L$ ) was calculated from the Thomson-Gibbs equation using the surface free energy per unit area of the crystal growth face,  $\sigma_e = 90 \times 10^{-3} \text{ J m}^{-2}$ , the enthalpy of melting per unit volume  $\Delta H_v = 286 \times 10^6 \text{ J m}^{-3}$  and  $T_m^c$  is the thermodynamic melting temperature of ethylene copolymer and  $T_m$  is the measured melting temperature<sup>[12]</sup>:

$$L = \frac{2\sigma_e}{\Delta H_v} \cdot \frac{T_m^c}{(T_m^c - T_m)} \quad (7)$$

The thermodynamic copolymer melting temperature ( $T_m^c$ ) is obtained from the equilibrium melting temperature ( $T_m^o = 418.7 \text{ K}$ ) by considering the mole fraction of crystallizable units in a random copolymer ( $x$ ) where  $\Delta H_u$  is the molar heat of fusion per repeat unit in the crystal,  $\Delta H_u = 8.284 \text{ kJ mol}^{-1}$ <sup>[13]</sup>.

$$\frac{1}{T_m^c} = \frac{1}{T_m^o} - \frac{R}{\Delta H_u} \cdot \ln x \quad (8)$$

The methylene sequence length ( $MSL$ ) was calculated from Eq. (9), which derived from the calibration curve generated by Keating *et al.*<sup>[14]</sup>.

$$-\ln(X) = \frac{135.5}{(T_m + 273)} - 0.331 \quad (9)$$

where  $X$  is the methylene mole fraction.

The statistics used to characterize each distribution were the weight average values ( $SCB_w$ ,  $MSL_w$  and  $L_w$ ), the standard deviation ( $\sigma$ ) and coefficient of variation ( $CV$ ).

### Results and Discussion

Figure 1 shows DSC heating curves obtained for LLDPEs after normal cooling (10 K/min), very slow continuous cooling (0.08 K/min), and thermal fractionation (4 K steps with 50 min isothermal). The melting temperatures ( $T_{m, 0.08}$ ) obtained after slow continuous cooling were higher than those obtained with normal cooling and the extent of shift of melting temperature was different for each LLDPE. The melting curves after fast cooling showed final melting at a much lower temperature for the ZN polymers, and in the case of the solution  $C_8$ -BPE-ZNsoln the higher temperature melting region exhibited a double melting endotherm, indicative of crystal rearrangement. The fast cooling is distinguished from the very slow cooling crystallization curves. Since the cooling rate used for slow cooling is 0.08 K/min, this slow continuous cooling method allows the system to be closer to its equilibrium state, and therefore polymer crystals approaching equilibrium are expected to form as in the thermal fractionation method<sup>[4]</sup>. These highly ordered crystals gave a higher melting temperature and showed no tendency to rearrange during heating, prior to melting. The thermal fractionation results provide a visualization of differing branch content fractions, and the distribution can be analyzed from the discrete peaks<sup>[15]</sup>. The discrete peaks provide a means of observing if rearrangement of crystals takes place, because if rearrangement occurs the peaks tend to merge. The loss of peak resolution can be readily observed. The melting curves after slow cooling provided a smooth distribution curve that can be analyzed in the same way as a molar mass distribution curve<sup>[16, 17]</sup>.

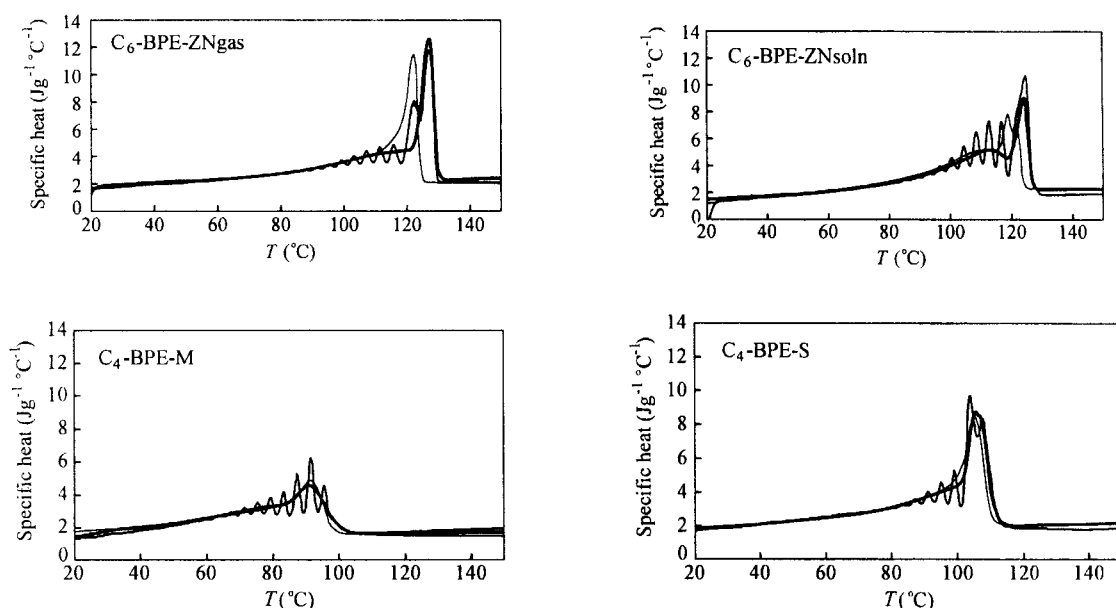


**Fig. 1** DSC specific heat curves for the polyethylenes after the three crystallization methods  
The thinner lines: cooling at a rate of 10 K/min; the normal lines: stepwise isothermal cooling; the thicker lines: cooling at a rate of 0.08 K/min

The degree of branching ( $B$ ) and crystallinity ( $X_c$ ) were calculated according to the equations, derived from TREF results<sup>[11]</sup>, and the  $SCB$  distributions obtained after very slow continuous cooling are presented in Fig. 2.

The average SCB values are also obtained from the curves, and listed in Table 2. Results for single site catalyzed polyethylenes having lower melting range are not shown here. Over the lower melting range, the calculations provide negative crystallinity data because of the lower starting and equilibration temperature of the DSC compared with TREF. This is a problem arising from the calibration, not from the DSC results. Another single site catalyzed polyethylene that we have studied has a peak melting temperature of 60 °C and very low crystallinity of about 12%. When slowly cooled to -50 °C the polyethylene continues to crystallize giving a final crystallinity of about 25%. Upon heating the polyethylene started to melt at about -20 °C. Such polymers are not suited to the present branching distribution analysis by our slow continuous cooling method. A broader temperature range calibration is required where Eqs. (4), (5), and (6) are modified to allow for crystallinity of highly branched polyethylenes that crystallize or continue to crystallize at sub-ambient temperatures.

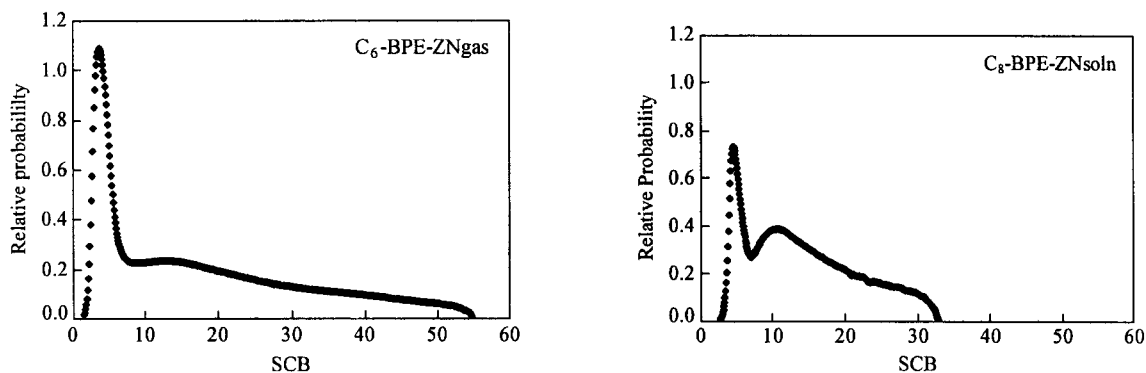


Fig. 2 SCB distributions for the Zeigler-Natta catalyzed gas phase and solution polyethylenes after slow continuous cooling

**Table 2.** The SCB, L, MSL and their distribution for the ethylene copolymers obtained by slow continuous cooling

| Properties                     | VLDPE2 | C <sub>6</sub> -BPE-ZN <sub>gas</sub> | C <sub>8</sub> -BPE-ZN <sub>soln</sub> |
|--------------------------------|--------|---------------------------------------|----------------------------------------|
| $T_{c, 0.08}$ (°C)             |        | 121.5                                 | 116.7                                  |
| $T_{m, 0.08}^P$ (°C)           |        | 126.7                                 | 112.7, 124.1                           |
| SCB <sub>w</sub> (1/1000C)     |        | 18.0                                  | 14.3                                   |
| $\sigma_{SCB}^a$               |        | 14.1                                  | 7.7                                    |
| CV <sub>SCB</sub> <sup>b</sup> |        | 0.78                                  | 0.54                                   |
| $x$                            |        | 0.964                                 | 0.971                                  |
| $T_m^c$ (°C)                   |        | 139.3                                 | 140.7                                  |
| $L_w$ (nm)                     |        | 12.9                                  | 9.8                                    |
| $\sigma_L^a$ (nm)              |        | 6.6                                   | 3.9                                    |
| CV <sub>L</sub> <sup>b</sup>   |        | 0.51                                  | 0.40                                   |
| $L^P$ (nm)                     |        | 20.6                                  | 9.3, 15.7                              |
| MSL <sub>w</sub>               |        | 118.9                                 | 91.5                                   |
| $\sigma_{MSL}^a$               |        | 88.4                                  | 54.5                                   |
| CV <sub>MSL</sub> <sup>b</sup> |        | 0.74                                  | 0.60                                   |

<sup>a</sup>  $\sigma$  = standard deviation; <sup>b</sup> CV = coefficient of variation

Branching density is expressed as the number of short chain branches per 1000 backbone carbon atoms. However, another way of expressing the data is into convert it into the methylene sequence length between branches. Crystallinity arises when the unbranched chain segments join the crystal face. During the crystallization

process, the branches are excluded from the crystals and the methylene sequence length will limit the lamellar thickness. Thus, MSL provides a number that reflects the ability of segments to crystallize. The composition distributions of the ethylene copolymers expressed in MSL are shown in Fig. 3.

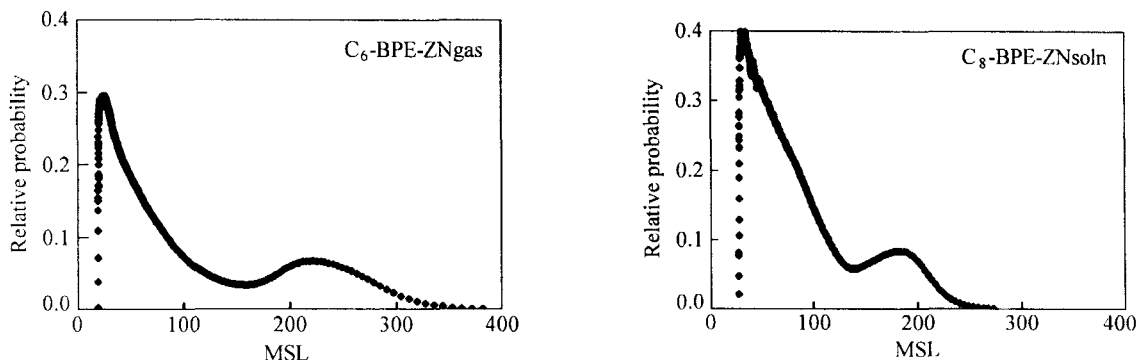


**Fig. 3** MSL distributions for the Zeigler-Natta catalyzed gas phase and solution polyethylenes after slow continuous cooling

The lamellar thickness of each LLDPE was calculated using the Thomson-Gibbs equation (Eq. 7), and the average lamellar thickness for each LLDPE was obtained from integration of the curves. Other researchers have used DSC data for calculation of lamella thickness<sup>[18]</sup>, and the use of  $T_m^c$  has been recommended<sup>[12, 13]</sup>. The curves were required to be integrated because the linear scale of temperature became not-linear after conversion to lamella thickness. Integration provided a linear scale that could be used to calculate averages and standard deviations. In the analysis, the thermodynamic copolymer melting temperature,  $T_m^c$ , was chosen as the limiting temperature for each of the polymers. This temperature is preferred to the equilibrium melting temperature ( $T_m^0$ ) for branched copolymers since the branches provide an absolute limitation on the melting temperature that can be reached by equilibration. The corresponding lamellar thickness distributions are shown in Fig. 4.

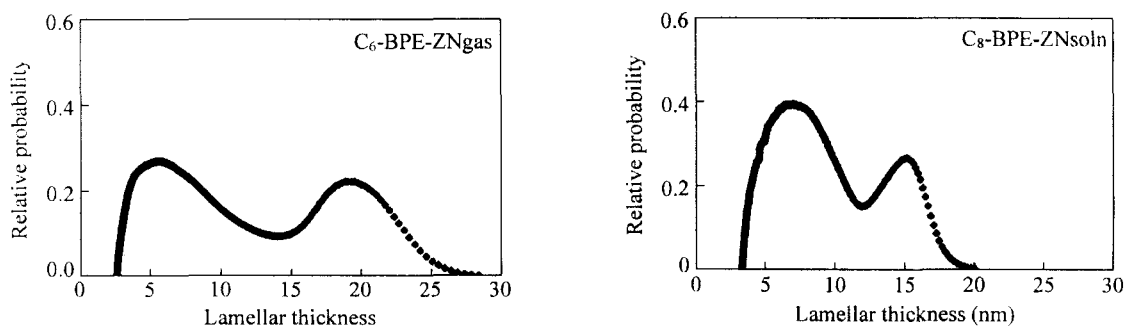


**Fig. 4** Lamella thickness distributions for the Zeigler-Natta catalyzed gas phase and solution polyethylenes after slow continuous cooling

Figure 5 shows the SCB distribution curves obtained after thermal fractionation. The distributions are composed of discrete fractions where each peak in the DSC curve has been converted into a bar of the bar graph by converting the peak temperature into SCB content and converting the peak area into total polyethylene by correction for the crystallinity for that level of branching. If a smooth curve were drawn through the tops of the bars, a graph the same as Fig. 2 would be obtained. Similarly, if the steps in the thermal fractionation procedure were decreased the discrete distribution graph would approach the continuous distribution. Figure 6 shows the analogous discrete distribution of the ethylene copolymers for MSL. Figure 7 shows the discrete distribution of the ethylene copolymers for lamellar thickness. These discrete distributions can still be analyzed to provide average parameters, though with lower resolution than those available from the continuous curves.

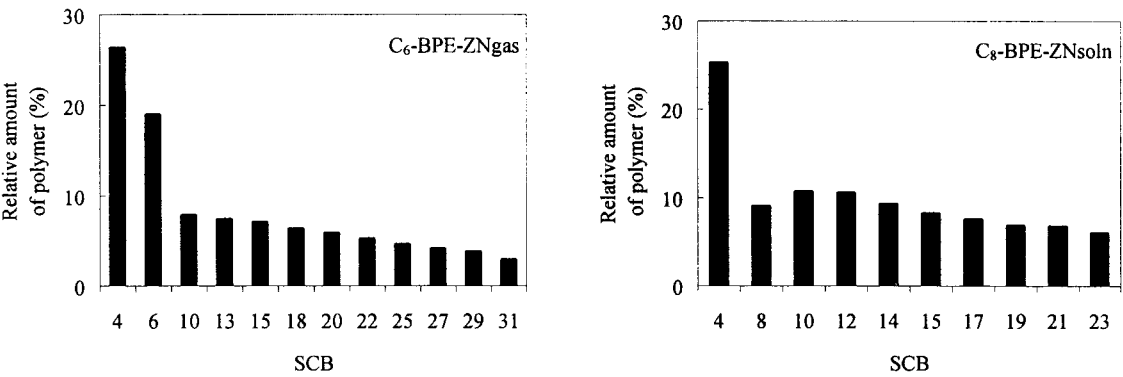


Fig. 5 SCB discrete distributions for the Zeigler-Natta catalyzed gas phase and solution polyethylenes after thermal fractionation

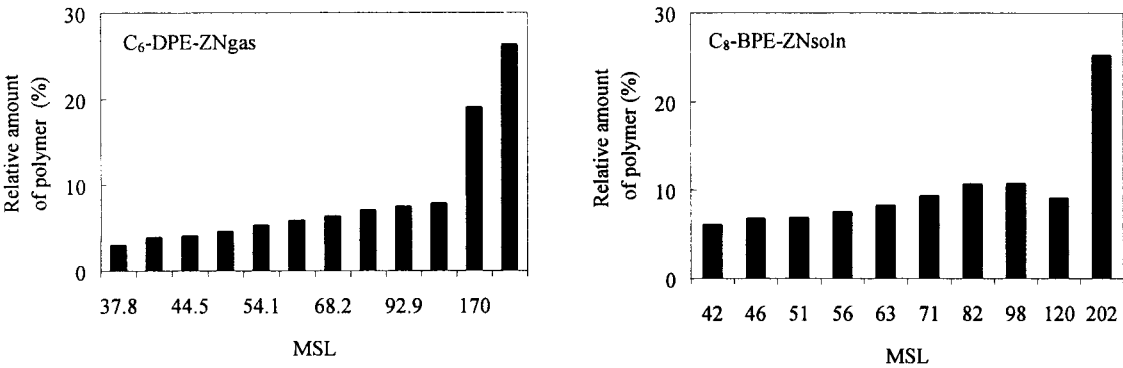


Fig. 6 MSL discrete distributions for the Zeigler-Natta catalyzed gas phase and solution polyethylenes after thermal fractionation

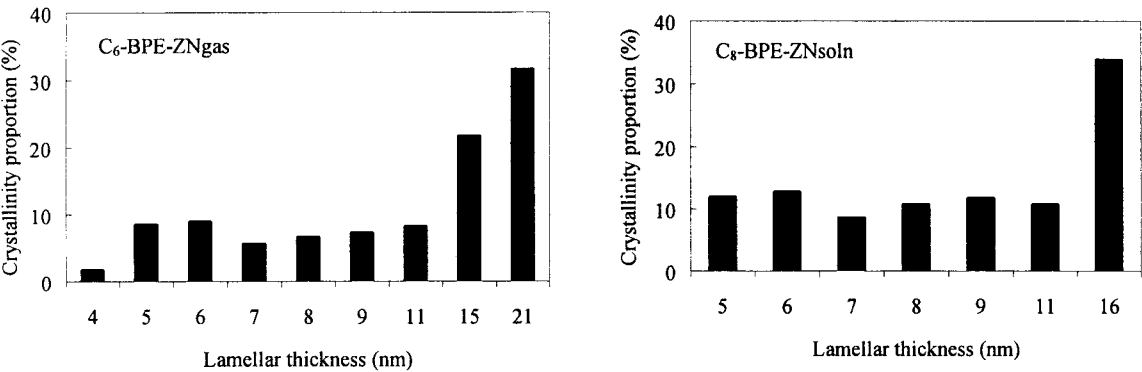


Fig. 7 Lamella discrete thickness distributions for the Zeigler-Natta catalyzed gas phase and solution polyethylenes after thermal fractionation

Table 2 shows the analyses of the continuous distribution curves. The peak crystallization and melting temperatures from the DSC scans after slow continuous cooling are listed first. The SCB weight average (SCB<sub>w</sub>) is 18.0 with a dispersity of 14.1 for C<sub>6</sub>-BPE-ZN<sub>gas</sub> and 14.3 and 7.7 for C<sub>8</sub>-BPE-ZN<sub>soln</sub>. The average short

branching distribution of the C<sub>8</sub>-BPE-ZNsolv was found to be similar to value of  $13.8 \pm 2.1$  as reported by Starck<sup>[5]</sup>.  $T_m^c$  were 139.3 and 140.7°C for C<sub>6</sub>-BPE-ZN<sub>gas</sub> and C<sub>8</sub>-BPE-ZNsolv, respectively. The weight average lamella thickness in each case is similar to values of 13.0 and 11.6 nm for two LLDPEs by TEM studies<sup>[7]</sup> and 12.9 and 8.6 nm from AFM<sup>[19]</sup>. Table 3 shows the analysis from the discrete distribution curves. The results are similar to those from the continuous curves, but the averages are based on a smaller number of data than available from the continuous curves.

**Table 3.** The SCB, L, MSL and their distribution for the ethylene copolymers obtained by thermal fractionation

| Properties VLDPE2              | C <sub>6</sub> -BPE-ZN <sub>gas</sub> | C <sub>8</sub> -BPE-ZNsolv |
|--------------------------------|---------------------------------------|----------------------------|
| SCB <sub>w</sub> (1/1000C)     | 12.6                                  | 11.9                       |
| $\sigma_{SCB}^a$               | 8.7                                   | 5.9                        |
| CV <sub>SCB</sub> <sup>b</sup> | 0.69                                  | 0.50                       |
| $L_w$ (nm)                     | 13.6                                  | 10.5                       |
| $\sigma_L^a$                   | 6.1                                   | 4.3                        |
| CV <sub>L</sub> <sup>b</sup>   | 0.45                                  | 0.40                       |
| MSL <sub>w</sub>               | 138.5                                 | 105.9                      |
| $\sigma_{MSL}^a$               | 82.4                                  | 69.4                       |
| CV <sub>MSL</sub> <sup>b</sup> | 0.59                                  | 0.65                       |

<sup>a</sup>  $\sigma$  = standard deviation; <sup>b</sup> CV = coefficient of variation

## CONCLUSIONS

DSC melting curves have been used to obtain short chain branching distributions using data from TREF for calibration of the branch content and crystallinity with melting temperature. The results from continuous slow cooling and thermal fractionation techniques are similar. The distributions were also represented as mean methylene sequence length and lamellar thickness distributions. Each of the distributions was used to provide typical averages, analogous to those obtained from size exclusion chromatography for molar mass. The weight average short chain branching, mean methylene sequence length between branches and lamellar thickness were obtained, with the standard deviation of each used as a dispersity index. The assumptions made for each of the calculations were discussed. The thermal fractionation data has been tested to ensure that recrystallization or rearrangement of crystals does not occur after the crystallization conditions are applied. A limitation was that the method was found to be suitable only for polyethylenes that start to melt sufficiently above ambient temperature that the DSC data can be correlated with TREF data.

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