

Note

A DSC method of measuring short-chain branching distribution in linear low density polyethylene

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Linear low density polyethylene (LLDPE) is a copolymer of ethylene with various α -olefins, such as butene-1, hexene-1, octene-1, and 4-methylpentene-1. The presence of small amounts of α -olefin introduces short chain branches (SCB) into the polyethylene backbone and modifies physical properties. LLDPE resins exhibit significantly improved mechanical properties (impact, tensile, and tear) at low and high temperatures compared to their conventional high pressure counterpart, low density polyethylene (LDPE) [1].

A significant amount of work has been carried out characterizing the molecular structure of LLDPE. Chain microstructure is reported to depend on five basic parameters: average weight percent of short chain branching distribution (SCBD), molecular weight, molecular weight distribution, and amount of SCB on a given molecular weight component [2]. It is generally recognized that SCBD is one of the principal factors that influence properties of LLDPE [3–5]. The extraordinary fracture toughness of LLDPE arises from extreme compositional heterogeneity of copolymers which comprise these LLDPE resins [6]. It is important to be able to measure SCBD in order to understand relationships between structure and properties in LLDPE.

A temperature rising elution fractionation (TREF) technique has been employed to provide data that reveals that SCBD of polyethylenes [7, 8]. In TREF, methylene contents of various fractions are measured and weight distribution as a function of temperature is taken as a measure of SCBD. Fractions with decreasing SCB contents elute at increasing temperatures. TREF is an effective method for measuring SCBD, but it is time consuming and requires special equipment.

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Differential scanning calorimetry (DSC) and differential thermal analysis (DTA) are popular, fast, and useful methods for investigating the crystallization process and crystalline morphology in polymers [9]. The existence of short-chain branching in LLDPE inhibits regular ordered packing of polymer chains. Crystallinity is reduced and polymer morphology is changed. These changes may be easily examined by DSC or DTA.

Over the last 15 years, many investigators have used DSC or DTA to try and elucidate the crystalline structure of polyethylenes. Briefly the following observations have been made:

(i) Bergstrom and Avela [10, 11] reported that widths of polyethylene thermograms from DSC or DTA were proportional to SCBDs.

(ii) Wlochowicz and Eder [12] proposed that lamella crystal thickness distribution of polyethylene can be determined from the DSC curve by use of the Thomson–Gibbs equation. However, because some SCBs are incorporated into the crystalline lattice especially for melt quenched polyethylene [13], the lamella crystal thickness distribution of polyethylene is different from the SCBD.

(iii) Burfield [14] performed a DSC study on LLDPE. Disruption of crystallinity by different comonomers was observed and the minimum fold chain length of the LLDPE lamella crystal was calculated.

(iv) Mirabella and Ford [4] fractionated LLDPE by TREF. DSC was used to characterize the whole polymer as well as the fractions of selected LLDPE resins. The broad and multimodal DSC melting trace of LLDPE resins was ascribed to a broad and multimodal SCBD.

(v) Hosoda [3] elucidated the molecular structure of LLDPE by combining solvent-gradient elution fractionation (SGEF) with TREF. DSC data of cross-fractions proved that a characteristic broad endothermic curve of LLDPE is attributable to its broad and multimodal chemical composition distribution. A DSC indicative index (DI) was proposed to express the chemical composition distribution of LLDPE more quantitatively. However, experimental results show that DI is also related to the distribution of lamella crystal thicknesses and is not directly related to the SCBD.

In this present study, Hosoda's experimental results were carefully re-analyzed and a DSC method is proposed that can directly measure SCBD of a SGEF fraction of LLDPE.

An LLDPE SGEF fraction is composed of various copolymers whose degree of SCB, melting temperatures, and crystallinities are quite different from each other. It is assumed that the response of a copolymer to a DSC treatment is largely independent of the response of the other copolymers present, provided the sample is crystallized slowly. The DSC response of different copolymers is assumed to be additive. According to Hosoda's results (table III of ref. 3) melting temperatures of TREF fractions of a previously made SGEF fraction (No. 10 of LLDPE (B)) are linear with degree of SCB. A plot of this TREF fraction melting point versus SCB

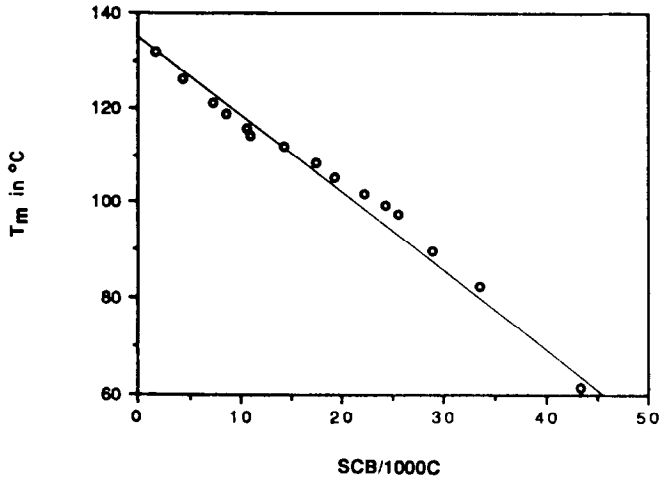


Fig. 1. Melting temperature as a function of degree of SCB.

(Fig. 1) fits a straight line given by

$$T_m / ^\circ\text{C} = 134 - 1.54(\text{SCB}/1000\text{C}) \tag{1}$$

where T_m in $^\circ\text{C}$ is the melting temperature, and $\text{SCB}/1000\text{C}$ is the degree of SCB per 1000 carbon atoms in the backbone. Crystallinity of individual TREF fractions of SGEF fraction No. 10 LLDPE (B) versus degree of SCB was also independently measured and found to have a linear relationship. Data is fitted by eqn. (2) and shown in Fig. 2, where $C\%$ is crystallinity

$$C\% = 82 - 1.27(\text{SCB}/1000) \tag{2}$$

Figure 3(a) is the original DSC curve of SGEF fraction No. 10 LLDPE

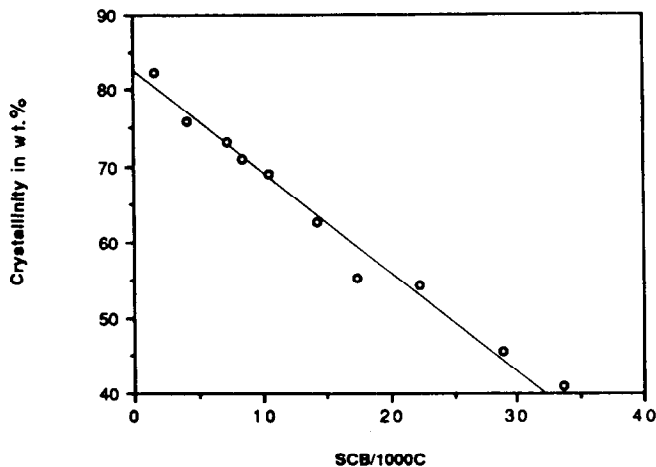


Fig. 2. Crystallinity as a function of degree of SCB.

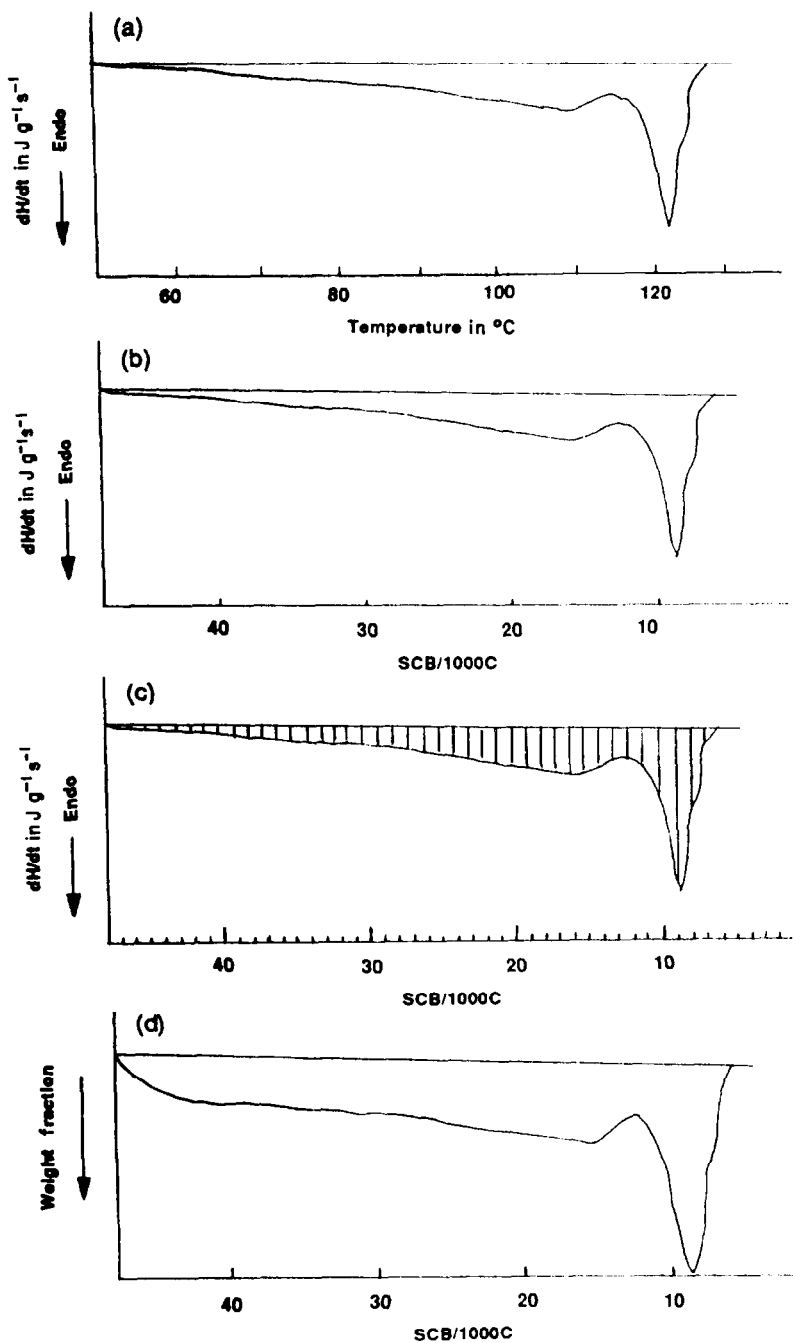


Fig. 3. (a) DSC trace of fraction No. 10 LLDPE (B). (b) DSC trace of fraction No. 10 LLDPE (B) with temperature scale transformed to SCB/1000C. (c) Transformed curve divided into strips of width 2 SCB/1000C units. (d) Weight distribution of the SCB in fraction No. 10 LLDPE (B).

(B) which has been slowly crystallized. Using eqn. (1), the temperature axis of a DSC curve can be transformed into a degree of SCB curve. Figure 3(b) depicts this transformation. The transformed curve is shown divided into strips whose widths are 2 SCB/1000C units in Fig. 3(c). The distance from the melting curve to the baseline was measured to determine the relative amount of crystallinity for different SCB components. Using the appropriate $C\%$ from eqn. (2), crystallinity for each component can be transformed into an amount of SCB. Therefore, the weight distribution of SCB of SGEF fraction No. 10 LLDPE (B) can be obtained and is shown in Fig. 3(d).

The method proposed here is an approximate one. We are ignoring any influence which different SCB components may have on each other. Although this method is used for an SGEF fraction, it is the first attempt to directly measure short chain branching distribution of a LLDPE from DSC data. We can assume that eqns. (1) and (2) hold for each SGEF fraction. Therefore, this method can be used for measuring SCBD of any whole slowly crystallized LLDPE polymer with the same α -olefin branch type.

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