# Long-Chain-Branching Index for Essentially Linear Polyethylenes

**R. N. Shroff* and H. Mavridis**

*Equistar Tecnology Center, 11530 Northlake Drive, Cincinnati, Ohio 45249*

*Received June 11, 1999*

ABSTRACT: Low levels of long-chain branching (LCB) in an otherwise linear polyethylene, such as HDPE or LLDPE, are known to affect dramatically the polymer melt rheological properties. However, reliable techniques to detect and quantify LCB at these levels (i.e., $\ll$1 LCB/1000 C) have not been available. In this work, the long-chain-branching index (LCBI) is developed for essentially linear, polydisperse polyethylenes, which are those containing a small level of LCB, such that the measured intrinsic viscosity is the same, within experimental error, to that calculated from MWD data, assuming the resins are linear. The long-chain-branching index (LCBI) is fundamentally related to the viscosity enhancement due to long-chain branching, and it is independent of molecular weight (MW) and molecular weight distribution (MWD). It is given by the relation: LCBI = $\eta_o^{0.179}/4.8[\eta] - 1$, where $\eta_o$ (P) is the zero shear viscosity at 190 °C, and $[\eta]$ (dL/g) is the intrinsic viscosity in trichlorobenzene at 135 °C. A suitable average molecular weight could substitute the intrinsic viscosity in this relation, if so desired. The numerical factors in the defining relation are derived on fundamental grounds such that the lowest value of 0.0 represents perfectly linear polyethylene. Various measures of LCB that have appeared in the literature, including the Dow rheology index (DRI) and those based on the activation energy of viscous flow, are critically examined and their limitations identified. The new index proposed here overcomes these limitations, as illustrated with a vast number of examples with commercial polyethylenes. The applicability of the LCBI for distinguishing LCB levels within conventional, free-radical polymerized LDPEs is also investigated.

## Introduction

The general objective of this work is to resolve the difficulty in quantifying long-chain branching (LCB) in essentially linear polyethylenes. These are the polyethylenes in which the LCB frequency is less than about 0.3/1000 carbon atoms. At such low levels of LCB, the conventional method[1] for determining LCB from the Zimm−Stockmayer equation (based on the combined use of size exclusion chromatography and intrinsic viscosity) is practically unusable. The Zimm−Stockmayer method estimates the LCB from the reduction in the hydrodynamic volume, which in turn is measured from the ratio $g'$, the ratio of intrinsic viscosity of the branched polymer, $[\eta]_B$ , to that of the linear polymer, $[\eta]_L$, of the same molecular weight. For small LCB levels, such as less than 0.3/1000 C, the ratio $g'$ is very close to 1.0, within experimental error, and determination of LCB becomes infeasible. Also, small variations in $g'$ cause large variations in LCB determination, as will be detailed later in this paper.

LCB is also measured by high-resolution nuclear magnetic resonance[2] (NMR). This technique also encounters difficulties at low LCB levels. One difficulty relates to the required correction[2] for short chain branching (typically two to six carbon atoms long in commercial polyethylenes) present in polyethylene. A second and more critical limitation is that the NMR approach cannot distinguish branch length for branches equal to or longer than six carbon atoms (thus, NMR cannot be used to characterize LCB in ethylene/octene-1 copolymers, which have hexyl groups as side branches).

One then is left with rheological properties of polymer melts which are known[3] to depend very sensitively on LCB, even at low levels of LCB. The central and difficult problem, however, is to separate the effect of LCB on rheology from the effect of molecular weight (MW) and molecular weight distribution (MWD). The specific objective of the present work is to report on the development of a long-chain branching index (LCBI) for whole, unfractionated, and essentially linear polyethylenes. The LCBI is largely independent of MW and MWD. The LCBI is derived from fundamental principles, but we examine critically its applicability for a wide variety of commercial polyethylenes and compare it to other approaches proposed in the litrature.

## Prior Studies

The possible existence of LCB in high MW fractions of essentially linear PEs (from the low-pressure process) was first suspected by Tung,[4] who found curvature in the plot of intrinsic viscosity, $[\eta]$, vs molecular weight for the high MW fractions. Hogan et al.[5] showed that presence of LCB in low pressure, unfractionated Phillips high density polyethylenes (HDPEs), raised low-shear melt viscosity without much affecting $[\eta]$ but offered no quantitative measure. As a result of LCB, parison sag and curtaining or draping in blow molding operations and sheet sag in the thermoforming process were considerably reduced (improved). Drott and Mendelson[6] found evidence of LCB in HDPEs based on the measured $[\eta]$ being lower than that calculated from MWD (GPC), assuming they are linear. Our results discussed below are in contrast with their observations. LCB was detected by Servotte and De Bruille[7] in the HMW portion of linear polyethylenes by the combined use of gel permeation chromatography (GPC) and on-line dilute solution viscosity. Locati and Gargani[8] introduced a relationship involving $[\eta]$, $\eta_o$, and a characteristic relaxation time, $\tau_o$, to calculate an index of LCB for irradiated HDPEs and conventional LDPEs. Rideal and Padget[9] used a combination of intrinsic viscosity and low shear viscosity data to illustrate generation of LCB in HDPE upon thermal/mechanical degradation. Com-

---

* Corresponding author

10.1021/ma9909354 CCC: $18.00

**Table 1. Rheological and Molecular Characteristics of Narrow MWD Resins ($M_w/M_n \sim 2-6$)**

| | MI 190 °C/2.16 kg (g/10 min) | nominal $\rho$ (g/cm$^3$) | $[\eta]_{meas}$ (dL/g) | $[\eta]_{calc}$(GPC) (dL/g) | $M_w \times 10^{-4}$ | $\eta_o \times 10^{-5}$ (190 °C) (P) | PDR | $E_R$ | $M_w/M_n$ | LCBI |
|---|---|---|---|---|---|---|---|---|---|---|
| Metallocenes | | | | | | | | | | |
| Exxon 3027 | 3.2 | 0.900 | 1.25 | 1.33 | 9.6 | 0.24 | 1.5 | 0.095 | 2.0 | 0.01 |
| Exxon 4011 | 2.2 | 0.886 | 1.35 | 1.44 | 10.8 | 0.36 | 1.5 | 0.070 | 2.0 | 0.01 |
| Exxon 5005 | 11 | <0.901 | 1.00 | 1.06 | 7.1 | 0.076 | 1.7 | 0.088 | 2.2 | 0.03 |
| Exxon 3028 | 1.2 | 0.900 | 1.46E[b] | 1.51 | 11.5 | 0.61 | 1.5 | 0.16 | 2.1 | −0.01 |
| Dow Affinity | 1.0 | 0.906 | 1.24 | 1.37 | 10.3 | 2.9 | 6.2 | 1.1 | 2.4 | 0.60 |
| Dow PF 1140 | 1.6 | 0.899 | 1.15 | 1.20 | 8.5 | 1.4 | 5.0 | 1.1 | 2.4 | 0.51 |
| NBS 1475 (linear PE) | | | | 1.04 | 5.3 | 0.062 | | | 2.9 | −0.02 |
| LLDPEs | | | | | | | | | | |
| Exxon LPX 1 granular | | | | | | 1.03 | 3.0 | 0.60 | | |
| Exxon LPX 1 pellets | 1.0 | 0.918 | 1.64 | 1.65 | 14 | 1.04 | 3.3 | 0.65 | 4.5 | 0.0 |
| Exxon LPX 2 granular | | | | | | 0.56 | 2.9 | 0.56 | | |
| Exxon LPX 2 pellets | 1.7 | 0.918 | 1.47 | 1.39 | 11 | 0.57 | 3.1 | 0.56 | 4.1 | 0.0 |
| Dow 2045 (1113513) | 1.0 | 0.918 | 1.54 | 1.60 | 13.8 | 1.4 | 4.2 | 0.96 | 4.2 | 0.13 |
| HDPEs | | | | | | | | | | |
| HD5831 (322EF) | 4.3 | | 1.28 | 1.20 | 9.5 | 0.25 | 3.1 | 0.71 | 5.7 | 0.0 |
| LS506 (H6FW53) | 8.2 | 0.949 | 1.10 | 1.06 | 7.7 | 0.11 | 2.4 | 0.43 | 3.7 | 0.0 |
| LS511 (H8CU53) | 13 | 0.950 | 1.06 | 1.04 | 7.5 | 0.081 | 2.4 | 0.47 | 3.9 | −0.02 |
| LS523 (H8JR53) | 25 | 0.956 | 0.894 | 0.837 | 5.5 | 0.038 | 2.2 | 0.41 | 3.7 | 0.02 |
| LS528 (H7AT53) | 34 | 0.950 | 0.856 | 0.782 | 5.0 | 0.027 | 2.3 | 0.51 | 4.3 | 0.02 |
| LS530 (H8AF53) | 44 | 0.950 | 0.820 | 0.762 | 4.9 | 0.022 | 2.1 | 0.48 | 4.1 | 0.0 |
| LS9010 granular | 2.1 | 0.952 | | | | 0.41 | 2.6 | | | |
| LS9010 (H1KC81) | 2.0 | 0.952 | 1.51 | 1.44 | | 0.42 | 2.8 | | 3.7 | −0.07 |
| LS9010 (H9AE47) | 1.4 | 0.952 | 1.49 | | | 1.2 | 4.9 | | 3.7 | 0.13 |
| LS9010 + 100 ppm peroxide | 1.3 | | 1.45 | | | ~1.4 | 5.9 | | | 1.20 |

[a] All resins made by Equistar, unless otherwise indicated. [b] Note: E = Estimated

bined use of light scattering, GPC, and viscometry by Agarwal et al.[10] showed evidence of small levels of LCB in HMW portions of commercial HDPEs. Bersted et al.[11] described HDPEs, which characteristically showed melt viscosity enhancement relative to linear polyethylene, as consisting of blends of long-chain branched and linear species and introduced a model to derive the melt viscosity behavior from MWD. Hughes[12] presented an equation for calculating LCB concentration in peroxide modified HDPEs using an incremental increase in activation energy for viscous flow over that for PE without peroxide. Similarly, Vega et al. [13] proposed a method to evaluate the possible presence of LCB based on the effect of temperature on the dynamic viscosity. Mavridis and Shroff[14] showed that low level of LCB in HDPEs are detrimental to the MWD ↔ rheology conversion scheme. A LCB index, DRI, based on rheological measurements for essentially linear polyethylenes of relatively narrow MWD ($M_w/M_n \sim 2-2.5$) is reported by Lai et al.[15] Shroff and Mavridis[16] have critically examined various measures of rheological polydispersity arising from differences in MWD and LCB. Wasserman and Graessley[17] have studied the applicability of MWD to rheology conversion scheme and flow activation energy to study the effect of MWD and LCB in polyethylenes. Wasserman[18] investigated the melt dynamic properties of various metallocene-catalyzed polyethylenes and derived a relaxation spectrum index, but the index apparently depends on MW, MWD, and LCB.

## Experimental Section

Data on a wide variety of samples are included in this report and are divided into three broad categories. The first group in Table 1 are resins of relatively narrow GPC−MWD ($M_w/M_n \sim 2.0-5.7$) and are considered as linear (as one can obtain among commercial grade resins).

The second group of resins in Table 2 are those with broad to very broad (bimodal) distribution HDPEs ($M_w/M_n \sim 6.6-30$). These resins are used in film and blow molding applications but have relatively lower rheological polydispersity elasticities ($E_R \sim 1.7-3.7$). The fundamental basis of the $E_R$ derivation and the significance of $E_R$ and other rheological polydispersity measures have been discussed elsewhere[16] and are briefly defined in Appendix A.

The third group of resins in Table 3 are broad distribution polyethylenes ($M_w/M_n \sim 6.0-14$) whose GPC−MWD's are deceivingly narrow while rheological distributions or relaxation time distributions are extremely broad ($E_R \sim 2.7-8.0$). Further characteristics of all these resins are detailed in Tables 1−3.

Melt index (MI) is a crude, inverse measure of $M_w$ and is measured using ASTM D1238 (2.16 kg/190 °C). Resin density, $\rho$, in most cases is nominal (i.e., as listed in the manufacturer's specification). A density of 0.96+ means no comonomer was added during polymerization.

Intrinsic viscosity, $[\eta]$, is calculated from the measured relative viscosity at a single nominal concentration of 0.2 g/dL in 1,2,4 trichlorobenzene (TCB) at 135°C. The calculation is performed iteratively using Martin's equation

$$\log(\eta_{sp}/c) = \log [\eta] + k_m[\eta]c \qquad (1)$$

where Martin's constant $k_m = 0.2138$. Various extrapolation procedures for calculating $[\eta]$ from the measured solution viscosity $\eta_{sp}$ are reviewed by Sakai,[19] who shows that Martin's equation can be used reliably to calculate $[\eta]$.

The gel permeation chromatograph (GPC) used in this work is a Waters model 150C with a refractive index detector. The column set used was Burdick & Jackson 10 $\mu$m particle size Ultrastyragel mixed bed and 1 × 500 Å 30 cm × 0.75 cm steel columns. The solvent is TCB, with a flow rate of 1.0 mL/min, column oven at 135 °C, and injection compartment at 145 °C. Intrinsic viscosity was calculated from the MWD and using Mark−Houwink's equation

$$[\eta] = KM_v^{\,a} \qquad (2)$$

where $K = 3.63 \times 10^{-4}$ and $a = 0.72$ for linear or essentially linear polyethylenes and $M_v$ is the viscosity average molecular weight.

**Table 2. Rheological Molecular Characteristics of Broad Distribution, Lower $E_R$ Resins**[a]

| | MI 190 °C/2.16 kg (g/10 min) | nominal $\rho$ (g/cm$^3$) | $[\eta]_{meas}$ (dL/g) | $[\eta]_{calc}$(GPC) (dL/g) | $M_w \times 10^{-4}$ | $\eta_o \times 10^{-5}$ (190 °C) (P) | PDR | $E_R$ | $M_w/M_n$ | LCBI |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | HDPEs−MVTR Film: Homopolymers | | | | | | |
| Oxychem M6210 | 0.91 | 0.96+ | 1.70 | 1.70 | 17 | 3.9 | 17 | 1.8 | 9.6 | 0.24 |
| Oxychem M6020 (295137) | | 0.96+ | 1.47 | 1.49 | 14 | 1.3 | 8.6 | 1.7 | 6.6 | 0.17 |
| HD6180 (I2PA53) | 1.18 | 0.96+ | 1.58 | 1.51 | 15 | 3.2 | 15 | 3.2 | 14 | 0.28 |
| Chevron 9659T (BO61397) | 1.04 | 0.96+ | 1.54 | 1.56 | 16 | 5.1 | 17 | 3.2 | | 0.42 |
| Chevron 9660 (C3003) | 0.78 | 0.96+ | 1.49 | 1.41 | 17 | 21 | 29 | 4.2 | 8.2 | 0.90 |
| | | | | HMW HDPE Copolymers | | | | | | |
| Nissan 3001 (10219) | 0.045 | | 2.72 | 2.43 | 30 | 26 | 19 | 2.4 | 30 | 0.07 |
| Taisox 9001 (83329) | 0.080 | | 2.47 | 2.24 | 27 | 27 | 15 | 2.1 | 30 | 0.19 |
| Mitsui 7000F (84464) | 0.041 | | 2.54 | 2.62 | | 32 | 33 | 3.4 | 37 | 0.19 |
| Cain 5005 (8903130011 SN2) | 0.058 | | 2.45 | 2.07 | 22 | 26 | 22 | 3.2 | 22 | 0.19 |
| Hoechst 9255 (8910 160015) | 0.086 | | 2.15 | 2.11 | 22 | 32 | 17 | 3.2 | 15 | 0.17 |
| LY 600 (POCH10) | 0.057 | | 2.43 | 2.34 | | 29 | 22 | 3.0 | 23 | 0.24 |
| | | | | MMW Copolymers: Blow Molding | | | | | | |
| Exxon 9856 (M92025011B) | 0.44 | 0.957 | 1.79 | 1.62 | 16 | 4.5 | | 2.6 | 14 | 0.19 |
| Oxychem 5840 AS (914412) | 0.39 | | 1.71 | 1.76 | 18 | 9.9 | 20 | 3.6 | 11.4 | 0.44 |
| LR 20810 (H2AK48) | 0.40 | | 1.65 | 1.75 | 18 | 15 | 36 | 3.7 | 14 | 0.61 |
| | | | | Miscellaneous (Phillips 66 Resins) | | | | | | |
| Mx 6050 (01−7−1500) | 6.3 | 0.96+ | 1.23 | 1.07 | 9 | 0.60 | 13 | 2.7 | 11 | 0.21 |
| Mx 6009 (01−7−1902) | 1.0 | 0.96+ | 1.69 | 1.53 | 16 | 6.3 | 21 | 2.9 | 13, 15 | 0.36 |
| Mx 6002 (01−7−1964) | 0.28 | 0.96+ | 2.13 | 2.12 | 24 | 18 | 23 | 2.9 | 12, 15 | 0.30 |

[a] All resins made by Equistar, unless otherwise indicated.

**Table 3. Rheological and Molecular Characteristics of Broad Distribution, High $E_R$ Resins**[a]

| | MI 190 °C/2.16 kg (g/10 min) | nominal $\rho$ (g/cm$^3$) | $[\eta]_{meas}$ (dL/g) | $[\eta]_{calc}$(GPC) (dL/g) | $M_w \times 10^{-4}$ | $\eta \times 10^{-5}$ (190 °C) (P) | PDR | $E_R$ | $M_w/M_n$ | LCBI |
|---|---|---|---|---|---|---|---|---|---|---|
| LR 920 | 0.34 | 0.946 | 1.64 | 1.55 | 15 | 35 | 36 | 4.8 | 9.3 | 0.88 |
| LR 732 (BIGR23) | 0.38 | 0.953 | 1.58 | 1.62 | 15 | 146 | 46 | 5.2 | 7.7 | 1.53 |
| 5602 (I1CA62) | 0.34 | 0.953 | 1.54 | 1.54 | 14 | 60 | 37 | 4.6 | 6.4 | 1.21 |
| 5602 (I8GC66) | 0.34 | 0.953 | 1.57 | 1.48 | 13 | 125 | 49 | 5.1 | 6.4 | 1.49 |
| 5602 granular: rheol ascending | | | 1.57 | | | 18 | 26 | 4.4 | | 0.76 |
| 5602 granular: rheol descending | | | 1.57 | | | 33 | 29 | 4.5 | | 0.96 |
| 5602 pellet: rheol ascending | | | 1.57 | | | 44 | 37 | 5.4 | | 1.07 |
| 5602 pellet: rheol descending | | | 1.57 | | | 96 | 43 | 5.4 | | 1.36 |
| 6009 (332KA) | 0.84 | 0.96+ | 1.49 | 1.32 | 12 | 13 | 28 | 4.2 | 10 | 0.76 |
| RMB 2871C (third pass extrusion of 6009) | 0.60 | 0.96+ | 1.44 | 1.34 | 12 | 2330 | 105 | 5.7 | 9.6 | 3.55 |
| 6008 (328AN) | 0.90 | 0.96+ | 1.45 | 1.48 | 10 | 18 | 30 | 4.3 | 6.0 | 0.88 |
| 6001 (I7SG51) | 0.28 | 0.96+ | 1.60 | 1.48 | 14 | 101 | 53 | 5.9 | 7.4 | 1.34 |
| 6001C (I8UR53) | 0.15 | 0.96+ | 1.80 | 1.76 | 17 | 624 | 82 | 6.8 | 6.9 | 1.88 |
| 5701G (358AH) | 0.0595 | 0.951 | 2.05 | 1.76 | 17 | 1060 | 142 | 7.8 | 9.8 | 1.78 |
| 6004 (I8WA52) | 0.28 | 0.96+ | 1.67 | 1.43 | 13 | 149 | 43 | 5.4 | 6.4 | 1.40 |
| 5603 (36NCK) | 0.34 | 0.946 | 1.52 | 1.51 | 14 | 22 | 34 | 3.9 | | 0.88 |
| experimental (V catalyst) | 0.19 | 0.9556 | 1.67 | 1.50 | 15 | 375 | 85 | 5.9 | 12 | 1.84 |
| experimental (V catalyst) | 0.14 | 0.9541 | 1.87 | 1.81 | 19 | 1970 | 123 | 6.2 | 12 | 2.40 |
| GA 8180−73 (M4MD2F) | 0.74 | 0.918 | 1.36 | 1.34 | 12 | 14 | 28 | 3.5 | 12 | 0.92 |
| Mitsui Neozex 2015M | | | | 1.30 | 10 | 2.24 | 12 | 2.3 | 6.6 | 0.46 |
| Visbroken 5071 (IH33040507) | 5.7 | | 0.974 | 0.985 | 6.8 | 0.263 | 6.0 | 0.88 | 4.0 | 0.65 |

[a] All resins made by Equistar, unless otherwise indicated.

Dynamic or oscillatory shear melt rheological data are obtained with a Rheometrics dynamic analyzer model RDA2 using parallel plates, in the radian frequency range 0.025−400 s$^{-1}$ . The strain was as high as 20% depending on the MI of the resin (10% for MI 0.2, 15% for MI ~0.2−1.0, and 20% for MI $\geqslant$ 1.5) but was verified to be in the linear viscoelastic region. The measurement temperature is 190 °C, except in cases where activation energy of flow is required, where the range is 150−210 °C, using a new sample at each temperature and using $N_2$ circulation through the sample oven for each measurement. All samples which may already contain antioxidants during their commercial pelletization operations are further stabilized by adding 2% of 50−50 antioxidant mixture of BHT and Irganox 1010 during compression molding at 150 °C of 25 or 50 mm diameter (depending upon the platen diameter) sample disks, which are prepared for ease of loading the sample into the rheometer and for minimizing sample degradation or cross-linking during measurements.

Even though the precautions above are taken to avoid chain extension or cross-linking during dynamic measurements on melts, some samples are susceptible to this tendency even when they are extra-stabilized and $N_2$ is flowing through the oven. For such materials, $\eta_o$ and other rheological data depend on whether the frequency sweep is ascending (from low to high) or descending (high to low)—see data in Table 3.

Limiting low-shear or zero-shear viscosity $\eta_o$ is estimated using the Sabia[20] equation fit of dynamic complex viscosity $\eta^*$ vs radian frequency (see Appendix B).

The rheological polydispersity measures ($E_R$, PDR) were derived from dynamic rheology data as described elsewhere[16] and defined briefly in Appendix A.

## Results and Discussion

**Basis or Justification for LCB/Cross-Linking Index.** Derivation of a long-chain-branching index from zero-shear viscosity and intrinsic viscosity data can be justified on fundamental grounds as follows. The zero-shear viscosity $\eta_o$ is known[3,21] to depend on molecular weight and long-chain branching through an equation of the form

$$\eta_o(M,\mathrm{LCB}) = [k_1(gM)^{a_1}]\Gamma_1(\mathrm{LCB}) \tag{3}$$

where $k_1$ and $a_1$ are constants, $\Gamma_1$ is the viscosity enhancement factor due to long-chain branching, and

$$g = \frac{<S^2>_\mathrm{B}}{<S^2>_\mathrm{L}} \tag{4a}$$

$$g' = \frac{[\eta]_\mathrm{B}}{[\eta]_\mathrm{L}} \tag{4b}$$

$$g' = g^{\epsilon} \tag{4c}$$

where $S$ is the radius of gyration, $\epsilon$ is a constant,[3,21] and the subscripts B and L denote "branched" and "linear", respectively. The intrinsic viscosity of a linear polymer is related to the molecular weight through

$$[\eta]_\mathrm{L} = K_2 M^{a_2} \tag{5}$$

Using eqs 4 and 5 to eliminate $M$ and $[\eta]_\mathrm{L}$ from eq 3 and rearranging gives

$$\frac{\eta_o^{a_2/a_1}}{[\eta]_\mathrm{B} g^{(a_2-\epsilon)}}\left(\frac{k_2}{k_1^{a_2/a_1}}\right) = \frac{\eta_o^{a_2/a_1}}{[\eta]_\mathrm{B} (g')^{(a_2/\epsilon-1)}}\left(\frac{k_2}{k_1^{a_2/a_1}}\right) = \Gamma_1^{a_2/a_1} \tag{6}$$

For very low levels of long-chain branching, $g = g' \approx 1$ in eq 6, and therefore

$$\Gamma_1^{a_2/a_1} = \frac{\eta_0^{a_2/a_1}}{[\eta]_\mathrm{B}}\left(\frac{k_2}{k_1^{a_2/a_1}}\right) \tag{7}$$

Equation 7 relates the viscosity enhancement factor, $\Gamma_1$, to the zero-shear viscosity, $\eta_0$, and intrinsic viscosity, $[\eta]_\mathrm{B}$. If the relation between the zero-shear viscosity and the intrinsic viscosity of linear polymers, $[\eta]_\mathrm{L}$, is known directly, i.e.

$$\eta_0 = k_3 [\eta]_\mathrm{L}^{a_3} \tag{8}$$

then, eq 7 for the viscosity enhancement factor can be stated as

$$\Gamma_1^{(1/a_3)} = \frac{\eta_0^{(1/a_3)}}{[\eta]_\mathrm{B}}\frac{1}{k_3^{(1/a_3)}} \tag{9}$$

where the relation between the constants of eq 8 and eqs 3, 5, and 7 is

$$k_3 = \frac{k_1}{k_2^{a_1/a_2}} \tag{10a}$$

$$a_3 = a_1/a_2 \tag{10b}$$

Since the viscosity enhancement factor, $\Gamma_1$, in eqs 7 and 9 is primarily dependent on long-chain branching, we can use eqs 7 and 9 to define a long-chain-branching index (LCBI)

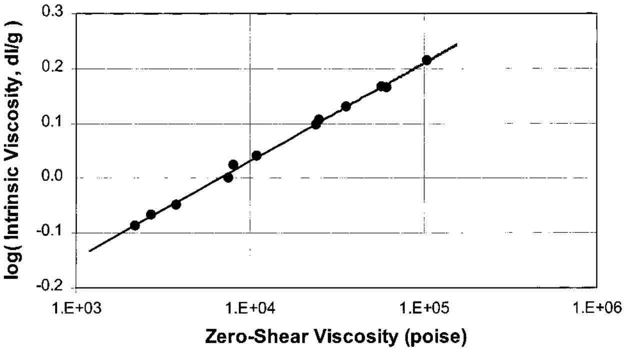

**Figure 1.** Intrinsic viscosity vs zero-shear melt viscosity for linear polyethylenes from Table 1 (correlation coefficient = 0.9986).

$$\mathrm{LCBI} \equiv \Gamma_1^{1/a_3} - 1 = \frac{\eta_0^{1/a_3}}{[\eta]_\mathrm{B}}\frac{1}{k_3^{1/a_3}} - 1 \tag{11}$$

so that LCBI = 0 for linear polymers with no long-chain branching. The constants in eq 11 for the definition of LCBI can be estimated in a number of ways:

(a) The first method uses experimental data to fit eq 8 for known, linear polymers. This is the approach adopted in the present work, as explained later.

(b) The second method uses established relationships, either for zero-shear viscosity vs intrinsic viscosity (eq 8), or for zero-shear shear viscosity vs molecular weight and intrinsic viscosity vs molecular weigt (eqs 3 and 5), again for linear polymers, to determine the constants, $k_1$, $k_2$, $a_1$, and $a_2$. The constants $k_3$ and $a_3$ required in eq 11 are then calculated from eq 10.

In the present work, we used approach a above, for whole polymers of varying MWD. The selection of such polymers which are strictly linear is not trivial, because a priori one cannot rule out the presence of a small level of LCB. We carefully selected low MI (MI 1−2) resins directly off the reactor (in granular form) and examined $G'$ and $G''$ data down to the lowest possible frequency and compared them with those for the pelletized resins. After ascertaining no change in $G'$ and $G''$ had occurred even at the lowest frequency, we expanded the list to include higher MI (lower MW) resins and assumed no LCB or cross-linking would occur in them on pelletization. The assumption is justified because when $[\eta]$ is plotted against $\eta_0$ for all these whole polymers, all points fall on a single line with a correlation coefficient of 0.9986 (Figure 1), giving the following relation:

$$\eta_0 = 6.7 \times 10^3 [\eta]^{5.6} \tag{12a}$$

or

$$k_3 = 6.7 \times 10^3\ \mathrm{P} \quad \text{and} \quad a_3 = 5.6 \tag{12b}$$

Substituting eq 12 into the defining relation for LCBI, eq 11, we then get

$$\mathrm{LCBI} = \frac{\eta_0^{0.179}}{[\eta]}\frac{1}{4.8} - 1 \tag{13}$$

The linear polymers obeying the relationship of eq 12 include Exxon Exact metallocene resins ($M_\mathrm{w}/M_\mathrm{n} \approx 2.0-$

2.2), LLDPEs ($M_w/M_n \approx 4.0-4.5$), and HDPE copolymers ($M_w/M_n \approx 3.7-5.7$)—the last two categories made using Ziegler–Natta catalysts. These are the polymers of Table 1 which are plotted in Figure 1 and for which LCBI = 0, within experimental error.

It is interesting to compare the coefficients of eq 13 that one may obtain by employing literature correlations. For fractions of linear polyethylenes with $M_w/M_n = 1.10-1.19$, Raju et al.[22] find the following relationships:

$$\eta_0 = 2.69 \times 10^3[\eta]^{5.1} \tag{14a}$$

$$[\eta] = 4.86 \times 10^{-4} {M_w}^{0.705} \tag{14b}$$

$$\eta_0 = 3.40 \times 10^{-14} {M_w}^{3.6} \tag{14c}$$

This translates to the following constants:

$$k_1 = 3.4 \times 10^{-14} \quad \text{and} \quad a_1 = 3.6 \tag{15a}$$

$$k_2 = 4.86 \times 10^{-4} \quad \text{and} \quad a_2 = 0.705 \tag{15b}$$

$$k_3 = 2.69 \times 10^{3} \quad \text{and} \quad a_3 = 5.1 \tag{15c}$$

Using the above constants in the defining relation for LCBI, eq 11, we get

$$\text{LCBI} = \frac{{\eta_0}^{0.196}}{[\eta]} \frac{1}{4.7} - 1 \tag{16}$$

based on eq 15, data of Raju et al.[22] Note that the coefficients of eq 16, based on the data of Raju et al.,[22] are very close to the coefficients of eq 13 of the present work and similar to that used earlier.[23] In general, however, it is recommended to employ data derived within one's own laboratory for the fit of eq 8 and the determination of the coefficients $k_i$, $a_i$.

The physical significance of LCBI in eq 13 derives from its relation to the viscosity enhancement factor, in eq 9. In other words, a polymer with a value of LCBI will have a zero-shear viscosity that is enhanced by the factor $(1 + \text{LCBI})^{a_3}$ due to the presence of long-chain branching.

Alternatively, one could use zero-shear viscosity and molecular weight data to define long-chain branching index in an analogous fashion. Starting from eq 3, the viscosity enhancement factor for essentially linear polyethylenes ($g \approx 1$) can be expressed as

$$\Gamma_1^{\ 1/a_3} = \left(\frac{\eta_0}{k_1 {M_w}^{a_1}}\right)^{1/a_3} \tag{17}$$

and therefore, a molecular weight-based long-chain branching index ($\text{LCBI}_{\text{MW}}$) can be defined by analogy to eq 11 as

$$\text{LCBI}_{\text{MW}} \equiv \Gamma_1^{\ 1/a_3} - 1 = \left(\frac{\eta_0}{k_1 {M_w}^{a_1}}\right) - 1 \tag{18}$$

However, this index was found to be more prone to error because of higher experimental error in $M_w$ measurements (see error analysis further below).

Implicit in the development of LCBI is the observation that $\eta_0$ is influenced chiefly by molecular weight and long-chain branching (eq 3) and only weakly, if at all, by MWD. This conclusion is supported by our data of Figure 1, by the work of Raju et al.[22] (whose data on fractions ($M_w/M_n = 1.1-1.2$) also obey a similar relationship), and by earlier studies cited by Graessley.[24]

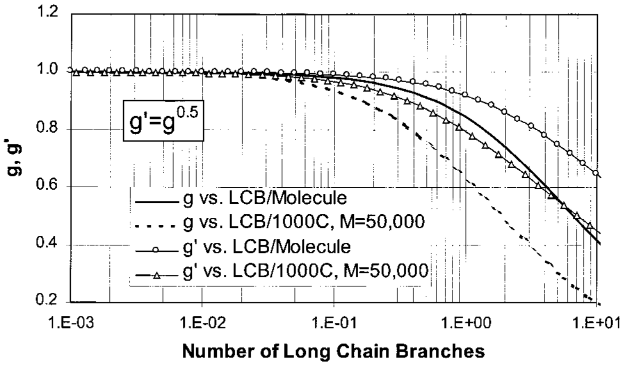

**Figure 2.** Dependence of the *g* factor on long-chain branching.

Note also that in the defining relations for the LCBI (eqs 11 and 18) the effect of long-chain branching on the radius of gyration is neglected, i.e., $g \approx 1$ in eqs 4 and 6. This simplification is justified for essentially linear polyethylenes, that is for linear polyethylenes with very low levels of long-chain branching, as explained below.

The dependence of *g* on LCB was derived theoretically by Zimm and Stockmayer[25] and is given by

$$\boldsymbol{g} = \frac{6}{n_w}\left[\frac{1}{2}\left(\frac{2 + n_w}{n_w}\right)^{1/2} \ln\left(\frac{(2 + n_w)^{1/2} + {n_w}^{1/2}}{(2 + n_w)^{1/2} - {n_w}^{1/2}}\right) - 1\right] \tag{19}$$

where $n_w$ is the weight-average number of long-chain branches per molecule. For a polyethylene chain, it is related to the long-chain branches per 1000 carbon atoms (LCB/1000 C) through:

$$n_w = (\text{LCB/1000 C})\,\frac{14000}{M} \tag{20}$$

where *M* is the molecular weight. Figure 2 shows a graphical representation of eq 19. It can readily be observed that the *g*-factor is nearly unity for LCB/1000 C < ~0.3. Therefore, using $g \approx 1$ for essentially linear polyethylenes (LCB/1000 C < ~0.3) is fundamentally justified.

Note also in Figure 2 that the *g′* factor, which is the experimentally measured quantity (see eq 4) is even closer to unity (which follows from eq 4c, due to $\epsilon \approx 0.5$ for low levels of LCB[26]). Therefore, for such low levels of long-chain branching, i.e., for essentially linear polyethylenes, it is practically impossible to estimate long-chain branching from eq 19 because the *g* factor is experimentally indistinguishable from unity. Additionally, as Figure 2 shows, the *g′* vs LCB curve changes very slowly in the region LCB/1000 C < ~0.3, or conversely, the LCB vs *g′* curve is very steep. This implies that a small change in *g′* (due to experimental error in either $[\eta]_B$ or $[\eta]_L$, for example) will cause a large change in LCB/1000 C.

**Error Analysis in LCBI or LCBI$_{\text{MW}}$.** Twenty-one measurements of intrinsic viscosity $[\eta]$ for LR 920 (a HDPE copolymer, Table 3) give a mean of 1.65 with deviation $\sigma_{n-1} = 0.047$ or a 6% error for the 95% confidence interval. Therefore, uncertainty in LCBI resulting from error in $[\eta]$ alone is 6%.

Twenty-three measurements and the resulting estimate of $\eta_o$ therefrom for HD 5602 (Table 3, a highly non-Newtonian flow curve even at low frequencies) give a mean $\eta_o$ of $1.01 \times 10^7$ P at 190°C with deviation $\sigma_{n-1} = 0.965 \times 10^7$ or a 20% error for 95% confidence limits. However, since the exponent of $\eta_o$ is 0.179, uncertainty in LCBI resulting from error in $\eta_o$ alone is only 1.7%, with a total error = 7.7%.

Nineteen measurements for Equistar-HD5205 (where Newtonian behavior is observed at lower frequencies) give $\eta_o = 3.5 \times 10^4$ P at 190 °C with deviation $\sigma_{n-1} = 0.204 \times 10^4$ or 12.2% error for 95% confidence limits. However, because the exponent for $\eta_o$ is 0.179, uncertainty in LCBI resulting from error in $\eta_o$ for these types of resins is only 1.6%, with a total error of 7.6%.

Forty-nine runs of GPC−MWD on LR920 (Table 3) give a mean $M_w = 1.5 \times 10^5$ with deviation $\sigma_{n-1} = 0.11 \times 10^5$ or 15.7% error for 95% confidence limits. Therefore, total error in $\mathrm{LCBI_{MW}}$ from $M_w$ and $\eta_o$ can be as high as 17.9%. Therefore, it is preferable to use eq 11 and measured intrinsic viscosity rather than one calculated from GPC−MWD data.

**LCBI vs DRI.** Lai et al.[15] have introduced a long-chain branching index, called DRI, based on $\eta_o$ and $\tau_o$ ($=1/\omega_o$ or $1/\dot{\gamma}_o$), derived using the Cross model (eq B-2 in Appendix B). DRI is defined as

$$\mathrm{DRI} = \left(3.65 \times 10^6 \frac{\tau_o}{\eta_o} - 1\right)/10 \qquad (21)$$

As stated by Lai et al.,[15] DRI is specifically designed for polymers with similar, narrow MWD and is not applicable if compared to polymers of differing MWD. The reasons for this restriction are pointed out in Appendix A, in the discussion of the limitations of the Cross model. As was discussed in ref 16, DRI is a measure of rheological polydispersity and as such it depends on both MWD and LCB. DRI could be used as a measure of LCB for polymers of known, same MWD, but any other measure of rheological polydispersity[16] could serve this purpose as well. The advantage of long-chain-branching index of the present work, compared to DRI, is that it does not require a priori knowledge of MWD, and it can be used to characterize LCB irrespective of MWD.

**LCBI vs Other Indexes.** Locati and Gargani [8] have proposed a deviation from the equation below as a measure of long-chain branching:

$$\log\left(\frac{\eta_o}{[\eta]^{2.84}\tau_o^{\,0.423}}\right) = \log K \qquad (22)$$

Here, log $K = 4.52$ for linear polymers, and $\eta_o$ and $\tau_o$ are derived from the rheological "curve" obtained using the Weissenberg rheogoniometer and using the Sabia equation. Presumably, the dynamic complex viscosity data are fitted to the Sabia equation. The equation was applied to irradiated HDPEs and three conventional LDPEs.

Since the index is based on fitting data to the original Sabia equation,[20] the value for A was presumably fixed at 2 for polyethylenes (see Appendix B). However, as we point out in Appendix B, when the MWD of the resin changes significantly, the fit is not satisfactory. Locati and Gargani[8] have no justification for the evolution or derivation of eq 22.

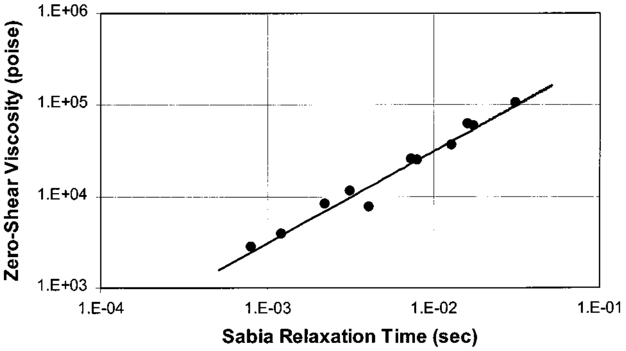

**Figure 3.** Zero-shear melt viscosity vs principal relaxation time for linear polyethylenes from Table 1 (correlation coefficient = 0.9859 − slope of the line = 1.0).

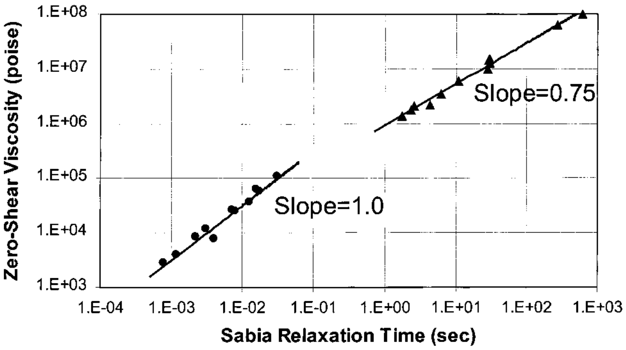

**Figure 4.** Zero-shear melt viscosity vs principal relaxation time for linear polyethylenes from Table 1 (slope = 1.0) and for polyethylenes with LCB from Table 3 (slope = 0.75).

Choosing resins which are strictly linear from among those listed in Table 1, we show that $\eta_o$ is directly proportional to $\tau_o$ (Figure 3) with a correlation coefficient of 0.9859

$$\eta_o = 3.23 \times 10^6 \tau_0^{\,1.01} \qquad (23)$$

provided the complex viscosity data at 190 °C in the radian frequency range 0.0251−400 s$^{-1}$ are fitted to Sabia's eq 1 with $AB = 0.72$ and $A$ is allowed to float. Substitution of eq 23 into eq 22 and rearrangement gives

$$\eta_o^{\,0.203}/[\eta] \equiv \text{constant} \qquad (24a)$$

for the linear polymers, and any deviation from eq 24a can be construed as a measure of LCB. However, note that there is more scatter in the data of Figure 3 vs those in Figure 1.

While eq 23 holds for linear resins, for many of the resins in Table 3 which contain LCB, $\eta_o$ is proportional to $\tau_o^{0.75}$ as shown in Figure 4. Substituting $\tau_o \sim \eta_o^{1/0.75}$ into eq 22 and rearranging gives

$$\eta_o^{\,0.154}/[\eta] \equiv \text{constant} \qquad (24b)$$

Therefore, Locati and Gargani's[8] measure of long-chain branching, eq 22, reduces to the relations of eq 24, which are similar in form (and in the value of the exponents) to the LCBI of the present work, eq 11.

Locati and Gargani[8] further imply that eq 22 is applicable to LDPEs and in particular to IUPAC LDPE samples **A**, **B**, and **C**. However, Meissner [27] originally noted that the mystery in these LDPEs is that despite similar behaviors in melt rheology in shear deformation, they had dissimilar behaviors in converging flow (entrance pressure drops) and extensional flow. Further the optical properties of blown films were superior and ability to make thin film gauge much better for IUPAC **B** and **C** vs those for **A**. The values of log *K* given by Locati and Gargani do not differ, within experimental error, from each other (log $K = 5.19$, 5.27, and 5.24, respectively. for IUPAC **A**, **B**, and **C**), yet the impression is given that value for log *K* can distinguish the level of LCB within LDPE with log $K = 4.8-5.6$ for LDPEs vs 4.52 for linear resins.

We will examine the applicability of LCBI to LDPEs later in this article and show its limitations, which are not obvious in ref 8.

**LCBI vs Activation Energy for Viscous Flow.** Activation energy, *E*, for viscous flow is affected[28,29] by chain flexibility, intermolecular interactions, concentration of polar groups, and side-chain branches. Polymers with high chain flexibility have low *E*, e.g., 3.6 kcal/mol for polydimethylsiloxanes and 6.3 kcal/mol for linear polyethylenes. Introduction of side branches into the chain increases the size of the chain segment and increases *E*. For example, *E* for very low density, linear polyethylenes (which are ethylene α-olefin copolymers) are as high as 8.4 kcal/mol. Presence of long-chain branching in polyethylene increases the activation energy further, but the situation becomes complex.[29,30] For example, one needs to shift the viscoelastic data not only horizontally to determine horizontal shift factor and the corresponding value $E_H$ (by shifting on frequency or shear rate or time scale), but also vertically (modulus or compliance scale), to determine the vertical shift factor and $E_V$. Failure to do so leads[31] to *E*, which is dependent on stress. For example, $E_H \simeq 14.7-16.0$ and $E_v \simeq 1.5-2.5$ kcal/mol for long-chain branched, conventional, free-radical polymerized LDPEs. Within LDPEs, neither $E_H$ nor $E_V$ showed[31] a trend with the extent of long-chain branching.

Therefore, the simplified equation proposed by Hughes[12] for HDPEs modified with up to 500 ppm peroxide is suspect:

$$\lambda = (E - 6.24)/7.93 \times 10^5 \qquad (25)$$

Here, *E* is the activation energy (kcal/mol), 6.24 is the value of *E* for the linear polymer and λ is the effective long-chain branching concentration. Hughes[12] obtained this relation from the data in the narrower frequency range $\omega \simeq 0.1-250\ \mathrm{s}^{-1}$ or in some cases even $1-250\ \mathrm{s}^{-1}$. Therefore, any possible thermorheological complexity[30,31] may not have been detected. Additionally, we will show that even a resin containing a small amount of LCB has an activation energy that cannot be distinguished, within experimental error, from that of a truly linear resin, as discussed below.

For example, a HDPE resin (6008 in Table 3), with LCBI = 0.88 calculated from eq 13, has an activation energy $E_H$, measured in the range 5.9−6.8 kcal/mol. Another resin, LS 9010 (Table 1), which is truly or perfectly linear (with LCBI = 0.0) also has activation energy of 5.9 kcal/mol. Another HDPE homopolymer, Mx 6009 (Table 2), with LCBI = 0.36, has an activation energy of 5.9 kcal/mol. Thus, activation energy does not show a trend with LCBI.

In a recent article, Vega et al. [13] recommended the calculation of a "LCB index" by subtracting the activation energy of flow of a linear polymer from that of a polymer with LCB. However, our data, discussed earlier, show that the value of the flow activation energy is influenced by the range of the temperature and frequency data employed for the calculation of the activation energy and by the presence of a thermorheological complexity in LCB polymers as discussed below. We also find, in agreement with Wasserman and Graessley,[17] that the absence of an enhanced flow activation energy does not necessarily preclude the absence of low levels of LCB, as shown earlier by the example of HD6008 and Marlex 6009. Therefore, while the enhancement of the flow activation energy can be attributed to the presence of LCB, the reverse is not necessarily true, and thus LCB cannot be identified with certainty from flow activation energy data.

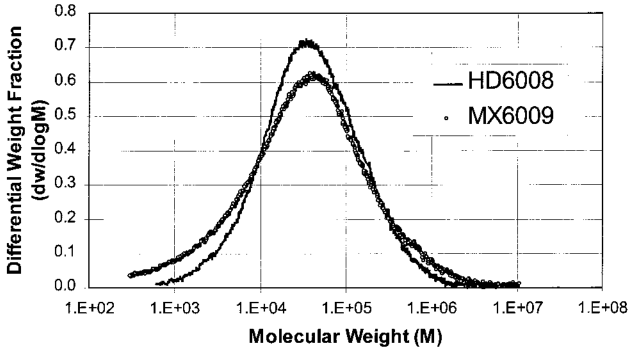

**Figure 5.** MWD of two polyethylenes. Equistar 6008 has a narrower distribution.

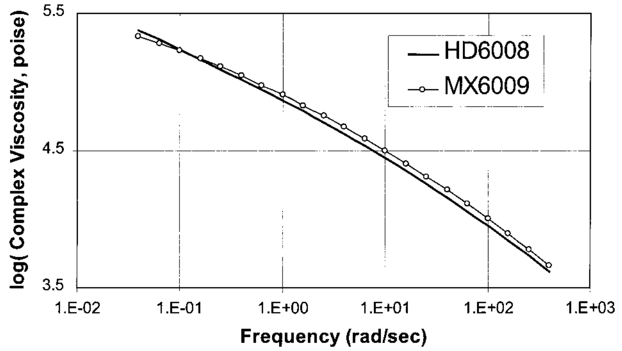

**Figure 6.** Complex viscosity at 190 °C vs radian frequency for the two polyethylenes of Figure 5. Equistar 6008 is more shear sensitive, despite its narrower MWD (from Figure 5).

To show that resin HD6008 (Table 3) indeed has a higher level of LCB compared to that for Phillips MX 6009 (Table 2), we compared the GPC−MWD for these two polymers (Figure 5). These data show that HD 6008 is narrower at both ends of the distribution. However, dynamic melt rheological data in Figure 6 indicate HD6008 is rheologically broader, with a higher $\eta^*$ at $\omega < 0.16\ \mathrm{s}^{-1}$ and a lower $\eta^*$ at $> 0.2\ \mathrm{s}^{-1}$.

We ascribe this reversal in GPC−MWD vs rheological distribution for HDPE pair as a manifestation of more LCB for HD6008. In particular, GPC distribution is deceivingly narrow for HD6008. Similar reversal in GPC vs rheology is seen when comparing a 1 MI, Dow PF1140, an ethylene−octene-1 copolymer containing LCB (narrow GPC distribution, broader rheological distribution) with a standard Ziegler catalyst, polymerized Dow 2045, an ethylene−octene-1 copolymer with a significantly reduced level of LCB (see Figures 7 and 8, and Table 1).

Other additional evidence for a higher LCB level in HD6008 vs Mx 6009 comes from lower shear viscosity for HD6008 in shear rate range $2-800\ \mathrm{s}^{-1}$ (Figure 9)

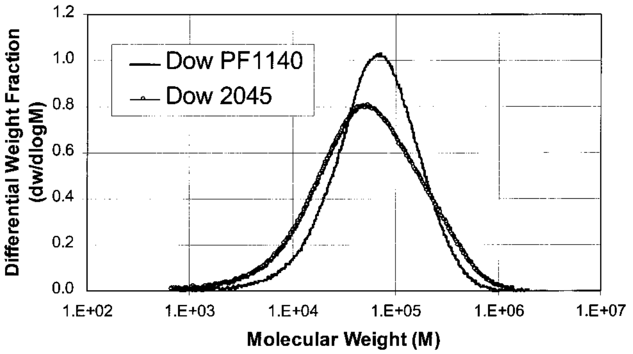

**Figure 7.** MWD of two polyethylenes. Dow Affinity with LCB has narrower MWD compared to Ziegler–Natta catalyzed resin (Dow 2045) of similar melt index.

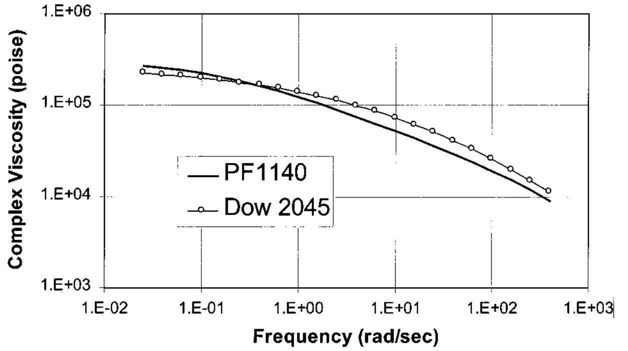

**Figure 8.** Complex viscosity at 190 °C vs radian frequency for the two polyethylenes of Figure 7. Dow Affinity is more shear sensitive, despite its narrower MWD (from Figure 7).

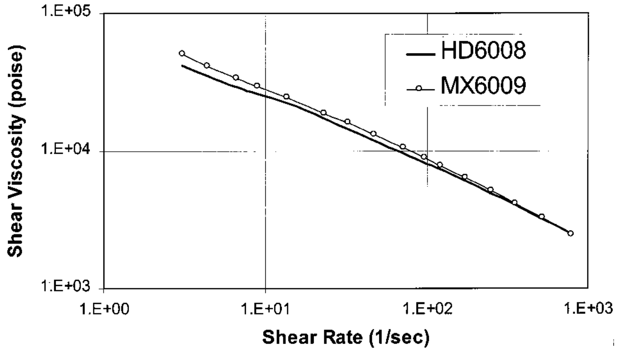

**Figure 9.** Corrected capillary shear viscosity data at 190 °C for Equistar 6008 and MX6009. Equistar 6008 shows lower shear viscosity (at high shear rates).

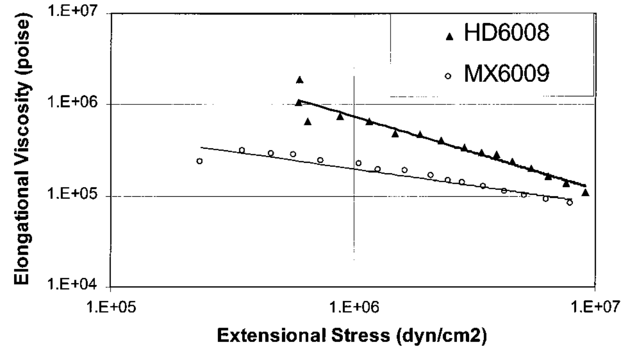

**Figure 10.** Apparent elongational viscosity data (from Cogswell's analysis) at 190 °C for Equistar 6008 and MX6009. Equistar 6008 shows higher elongational viscosity.

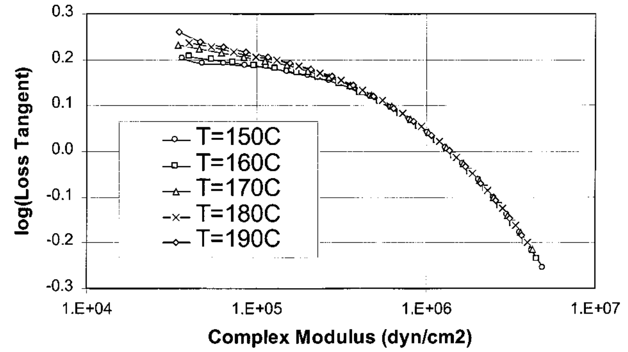

**Figure 11.** Loss tangent vs complex modulus at different temperatures for an LLDPE treated with 150 ppm peroxide. Data indicate thermorheologically complex behavior.

**Table 4. Horizontal and Vertical Activation Energies for a LLDPE (1.0 MI, 0.918 $\rho$, Ethylene–Hexene-1 Copolymer) Modified with 150 ppm Peroxide [GA 6010-30 (MOGV2C) + 150 ppm Peroxide][a]**

| radian frequency range ( $s^{-1}$) | $E_H$ (kcal/mol) | $E_V$ (kcal/mol) |
|---|---|---|
| 0.0251–398 | 9.3 ±1.3 | 0.92 ± 0.43 |
| 0.1–398 | 8.9 ± 0.89 | 0.66 ± 0.39 |
| 1–398 | 8.7 ± 0.34 | 0.45 ± 0.24 |
| 10–398 | 8.4 ± 0.17 | 0.44 ± 0.24 |
| 1–10 | 10.5 ± 0.74 | 1.1 ± 0.65 |
| 0.0251–10 | 15.8 ± 2.0 | 2.3 ± 1.4 |
| 0.0251–1 | 24.3 ± 1.9 | 8.5 ± 1.9 |

[a] Data measured at 150, 160, 170, 180, and 190 °C.

and yet higher extensional viscosity (Figure 10) calculated using Cogswell's analysis.[32,33]

**Thermorheological Complexity in Determining *E*.** In support of our view above that the activation energy of viscous flow may not be reliably used in calculating long-chain branching concentration, we present data here on a linear low-density polyethylene (hexene-1 copolymer, 1.0 MI, 0.919 $\rho$) modified with 150 ppm peroxide—well within the range examined by Hughes.[12]

The data are presented in the form of tan $\delta$ vs $G^*$ [$\equiv(G'^2 + G''^2)^{0.5}$] so that a trend can be seen in $E_V$. In Figure 11, one can see a clear lack of data superposition at low frequency or low $G^*$. A similar trend exists in the plot of tan $\delta$ vs $\omega$ (not shown here). The implication of the lack of superposition in practice is that the computation of $E$ depends highly on the frequency range of the data. As shown by the results in Table 4, $E_H$ varies from 8.4 to 9.3 if the data are in $\omega$ range 0.025–398 whereas it can jump to as high as 24 if the $\omega$ range is 0.0251–1 $s^{-1}$. A similar disparity exists in the vertical shift factor $E_V$. This behavior is called thermorheological complexity and implies different mechanisms of flow corresponding to the differing molecular structure exhibited at low vs intermediate vs high frequencies.

**Significance of Long-Chain Branching.** The presence of even a small level of LCB dramatically affects melt rheological properties as indicated above with respect to comparison of HD6008 vs Mx 6009. For example, LCBI is 0.88 vs 0.36, $E_R$ is 4.3 vs 2.9, and PDR is 30.0 vs 21, respectively, for this pair of HDPEs. Let us also examine the distribution of relaxation times for HD6008 vs Mx6009 in Figure 12. The data show a dramatic increase in long relaxation times for a resin containing small level of LCB (HD6008), such that the peak in the relaxation spectrum is not even observable within the experimental data range. The normalized relaxation spectrum shown in Figure 12 is derived from

**Table 5. Properties for Whole Polymer LDPE Resins (Reference 44)**

| resin | MI | $\rho$ (g/cm$^3$) | $[\eta]_{\mathrm{measd}}$ (dL/g) | $\eta_o \times 10^{-4}$ (190 °C) (P) | die swell @ shear stress = $7.5 \times 10^5$ dyn/cm$^2$ (%) | corrected GPC data (Drott−Mendelson procedure) $M_n \times 10^{-4}$ | $M_w \times 10^{-4}$ | $M_w/M_n$ | $\lambda \times 10^4$ | $g'$ | eq 26 LCBI$_{\mathrm{LDPE}}$ ($a_2 = 0.7$) $\epsilon = 0.5$ | $\epsilon = 0.65$ | $\epsilon = 0.8$ | $\epsilon = 1.0$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I−NA205 | 2.8 | 0.920 | 0.80 | 5.2 | 95.7 | 2.4 | 37 | 15.4 | 1.7 | 0.24 | 2.22 | 1.0 | 0.52 | 0.19 |
| J-NA458 | 1.9 | 0.922 | 0.80 | 8.5 | 74.0 | 1.6 | 14 | 8.6 | 0.78 | 0.45 | 1.73 | 1.11 | 0.80 | 0.56 |
| III−NA218 | 1.4 | 0.926 | 0.82 | 5.5 | 63.3 | 2.1 | 8.6 | 4.1 | 0.46 | 0.61 | 1.18 | 0.86 | 0.69 | 0.55 |

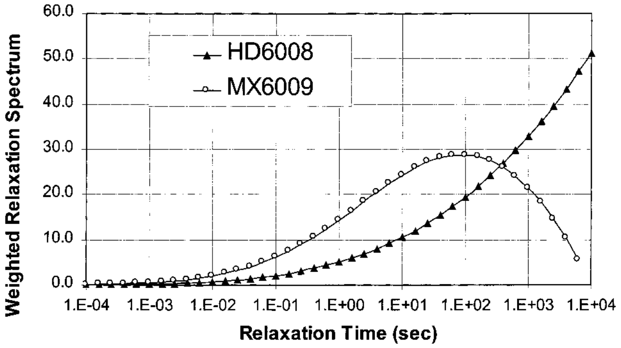

**Figure 12.** Weighted viscoelastic relaxation spectrum ($\tau H(\tau)\eta_o$) for Equistar 6008 and MX6009 derived from dynamic frequency sweep data ($G'$, $G''$). Equistar 6008 shows a broader relaxation spectrum.

storage modulus $G'$ and loss modulus $G''$ data using a regularization procedure[34] with quadratic programming.

It is well-known that LCB improves processability parameters, such as ease of extrusion, because of lower viscosity at high shear rates and high melt strength or low sag because of higher viscosity at low shear rates. In addition, we have already shown earlier[35] the large effect of LCB on crystallization rates which difference in turn may alter the resulting solid-state structure.

**Long-Chain Branching in Conventional LDPEs.** Conventional LDPEs, even those with the narrowest MWD and lowest level of LCB, contain long-chain branching such that the intrinsic viscosity of either the whole polymer or even its fractions is lower than that of the linear polymer of the same molecular weight. The reduction in intrinsic viscosity results from decreased radius of gyration for LDPE. Therefore, quantification of LCB in whole LDPEs is done by established methods[36,37] involving determination of apparent MWD using GPC in combination with whole polymer intrinsic viscosity.

The question arises as to whether the LCBI applies to LDPE. This question is addressed in Table 5 for the LDPEs of ref 40. The amount of LCB is such that the intrinsic viscosity is affected, and this effect is taken into account through the factor $g'$ (eq 4b). Therefore, the LCBI definition of eq 11 needs to be expressed as follows (from right-hand-side of eq 6 and left-hand-sided of eq 11):

$$\mathrm{LCBI}_{\mathrm{LDPE}} \equiv \Gamma_1^{(1/a_3)} - 1 = \frac{\eta_0^{(1/a_3)}}{[\eta]_{\mathrm{B}}(g')^{(a_2/\epsilon - 1)}} \frac{1}{(k_3)^{(1/a_3)}} - 1 \tag{26}$$

The parameters $k_3$ and $a_3$ of eq 12 were used in eq 26. The parameter $\epsilon$ in eq 26 is also required for the calculation of LCBI$_{\mathrm{LDPE}}$. Various values of $\epsilon$ are considered in Table 5. For $\epsilon = 0.5$, we get the expected LCBI$_{\mathrm{LDPE}}$ trend, resin **I** > resin **J** > resin **III**, with resin **I**, which has the highest LCB (lowest $g'$) having the highest LCBI$_{\mathrm{LDPE}}$. However, the expected trend is lost for higher $\epsilon$ values (even at $\epsilon = 0.65$, used by Mirabella and Wild[38]). It has been reported that the $\epsilon$ parameter changes with the level of LCB, from a value of 0.5 for perfectly linear polymers, to ~0.8 for medium LCB and ~1.0 for high LCB.[27] Mirabella and Wild[38] used a value of 0.65 for commercial LDPEs, and Pang and Rudin[1] used a value of 0.7.

Examination of the LCBI$_{\mathrm{LDPE}}$ values in Table 5 shows that for realistic values of $\epsilon$, i.e., greater than 0.5, the values of LCBI do not relate with direct measures of LCB (obtained from intrinsic viscosity and GPC data). More work is required to settle unambiguously the question of whether the long-chain branching index as derived this work, applies to LDPE. Note, however, that the primary purpose of LCBI is for essentially linear polyethylenes, in which the LCB is not detectable by solution measurements (in LDPE the LCB is already detectable and quantifiable through solution measurements).

## Concluding Remarks

A long-chain branching index (LCBI) is developed for essentially linear polyethylenes. The LCBI requires only zero-shear melt viscosity (190°C) and intrinsic (dilute solution) viscosity and is independent of molecular weight (MW) and molecular weight distribution (MWD). Essentially linear polyethylenes are those which contain low levels of LCB (may or may not contain short-chain branches) such that the measured intrinsic viscosity is the same, within experimental error, to that calculated from molecular weight distribution data. Advantages of our LCBI over other such measures in the literature, including the Dow rheology index (DRI) and that based on activation energy of viscous flow, are highlighted. The LCBI may not be applicable for characterizing the level of LCB in some conventional (free-radical polymerized) whole LDPEs.

**Acknowledgment.** Experimental rheological data were measured by L. Milawski, R. McPherson, and R. VanWinkle. GPC−MWD and intrinsic viscosity data were measured by L. Barilla and S. Barnett. Helpful discussions with Dr. F. Mirabella are appreciated.

## Appendix A: Rheological Polydispersity Measures $E_{\mathrm{R}}$ and PDR

The definition and justification of these measures of rheological polydispersity was given in ref 16, but a brief description is included here for completeness. $E_{\mathrm{R}}$ and PDR utilize linear viscoelastic data of storage modulus, $G'$, loss modulus, $G''$, and complex viscosity, $\eta^*$, in the frequency range of 0.0158−400 rad/s. Both $E_{\mathrm{R}}$ and PDR are independent of MW and temperature of measurement, but they are influenced by MWD and LCB.

$E_{\mathrm{R}}$, a measure of rheological polydispersity at the high MW end, is extracted from $G'$ vs $G''$ data at the two lowest decades of frequency

$$E_R = [C_1 G']_{\text{at } G''_{\text{ref}}} \quad \text{(A-1)}$$

where $G''_{\text{ref}}$ is selected to be a low modulus value (corresponding to low frequencies) and $C_1$ is a normalization constant. For polyethylene melts, good results have been obtained with $G''_{\text{ref}} = 5000$ dyn/cm$^2$ and $C_1 = 1.781 \times 10^{-3}$ cm$^2$/dyn. When the available data do not extend down to $G''_{\text{ref}}$, use is made of the fact that a log−log plot of $G'$ vs $G''$ is nearly linear in that region and thus extrapolation is possible.

PDR is derived from the data of complex viscosity vs complex modulus, covering the entire range of measured frequencies from 0.0158 to 400 rad/s. The complex viscosities $\eta_1^*$, $\eta_2^*$ and $\eta_3^*$ are calculated at three values of complex modulus, $G^*_1$, $G^*_3$, and $G^*_2 = (G^*_1 G^*_3)^{1/2}$, by extrapolation or interpolation as necessary. The PDR index is then calculated as

$$\text{PDR} = \frac{\eta_1^*}{\eta_3^*} \cdot \frac{(\eta_1^* \eta_3^*)^{1/2}}{\eta_2^*} \quad \text{(A-2)}$$

The first term in the right-hand-side of eq A-2 is a measure of shear sensitivity. The second term in the right-hand-side of eq A-2 is a measure of the curvature of the viscosity curve, with a larger curvature corresponding to smaller polydispersity. The reference modulus values $G^*_1$ and $G^*_3$, are typically selected as $G^*_1 = 1.95 \times 10^4$ dyn/cm$^2$ and $\log(G^*_3/G^*_1) = 2$ for essentially linear polyethylenes, whereas $G^*_1 = 10^4$ dyn/cm$^2$ and $\log(G^*_3/G^*_1) = 1.5$ for high-pressure long-chain-branched polyethylenes. These values were selected so that they cover as wide a range as possible and, at the same time, so that they are accessible experimentally for the majority of materials of interest.

## Appendix B: Zero-Shear Viscosity Estimation Using Sabia, Generalized Cross-Carreau, or Cross Models

The limiting low-shear or zero-shear viscosity $\eta_o$ is estimated using the Sabia[20] equation fit of dynamic complex viscosity $\eta^*$ vs radian frequency $\omega$

$$\log(\eta^*/\eta_o) = (\eta^*/\eta_o - A) \log[1 + (\omega/\omega_o)^B] \quad \text{(B-1)}$$

with the parameters $\eta_o$, $\omega_o$, $A$, and $B$, where $\omega_o$ is the inverse of the principle relaxation time $\tau_o$. Sabia originally kept the value of $A$ fixed at 2 for polyethylenes and polypropylenes. Nakajima[39] proposed and Shida and Cote[40] later implemented a computer program to let the $A$ value float because of the wide range of MWD encountered. The value of product $AB = 0.72$, which is related to the limiting slope of $\eta^*$ vs $\omega$ ($-AB$), is kept fixed, based on the fundamental consideration from Graessley's theory,[41] which predicts a steady flow viscosity having a constant limiting slope with respect to shear rate and from the consideration that complex viscosity vs $\omega$ is analogous to steady flow viscosity vs shear rate behavior. Sabia,[20] Nakajima,[39] and Shida and Cancio[42] originally selected a final slope value of 0.6667, which was later increased to 0.72 because viscosity vs frequency and viscosity vs shear rate data on some polyethylenes did not fit the above equation to a desired accuracy even when $A$ was allowed to float.

The Cross model has been used recently by Plumley et al.[43] and Lai et al.[15] to derive a long-chain branching index. The Cross model is

$$\eta^*/\eta_o = 1/[1 + (\omega/\omega_o)^{1-n}] \quad \text{(B-2)}$$

In the limit of high frequencies, the Sabia equation (eq B-1) reduces to

$$\eta^*/\eta_o = (\omega/\omega_o)^{-AB} \quad \text{(B-3)}$$

whereas the Cross equation reduces to

$$\eta^*/\eta_o = (\eta/\eta_o)^{n-1} \quad \text{(B-4)}$$

Therefore, $AB$ of the Sabia equation corresponds to $1 - n$ of the Cross equation. The Cross model is a special case of the Sabia equation, because its use implies that the value of $A$ in eq B-1 is fixed at 1.5 (from eq B-2, when $\omega/\omega_o = 1$ and $\eta^*/\eta_o = 0.5$; from eq B-1, for $\eta^*/\eta_o = 0.5$, $\omega/\omega_o = 1$, and $A = 1.5$). The use of the Cross model is, therefore, less satisfying because it allows the value of limiting slope ($AB$) to float and in effect lets $A$ remain fixed at 1.5. Plumley et al.[43] do not succeed in getting a master curve for their 65 Insite technology polymers presumably because of the deficiency of the Cross model in handling polymers of varying MWD as well as LCB.

The aforementioned limitation of the Cross model, of course, can be overcome by using a generalized Carreau model[45]:

$$\eta^*/\eta_o = \left[1 + \left(\frac{\omega}{\omega_o}\right)^m\right]^{(n-1)/m} \quad \text{(B-5)}$$

The constant $n$ is related to $AB$ as in the Cross model above, i.e., $AB = 1 - n$; additionally, the constant $m$ can be related to the Sabia parameter $A$ through the relation

$$A = 2^{-(AB)/m} + \frac{AB}{m} \quad \text{(B-6)}$$

Since the generalized Carreau model does not offer an added advantage, we decided to continue to use the Sabia equation to estimate $\eta_o$ required in the development of LCBI.

## References and Notes

(1) Pang, S.; Rudin, A. *Polym. Mater. Sci. Eng.* **1991**, *65*, 95−96.
(2) Yan, D.; Wang, W.J.; Zhu, S. *Polymer* **1999**, *40*, 1737−1744.
(3) Graessley, W. W. *Acc. Chem. Res.* **1977**, *10*, 332−339.
(4) Tung, L. H. *J. Polym. Sci.* **1959,** *36*, 287−294.
(5) Hogan, J. P.; Levett, C. T.; Werkman, R. T. *SPE J.* **1967**, (Nov) *23*, 87−89.
(6) Drott, E. E.; Meldelson, R. A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1971**, *12* (1), 277−281.
(7) Servotte, A.; De Bruille, R. *Makromol. Chem.* **1975**, *176*, 203−212
(8) Locati, G.; Gargani, L. *Proc. 7th Int. Congr. Rheol.* **1976**, 520−521.
(9) Rideal, G. R.; Padget, J. C. *J. Polym. Sci., Symp.* **1976**, *57*, 1−15.
(10) Agarwal, R.; Horsk, J.; Stejskal, J.; Quadrat, O.; Kratochvil, P. *J. Appl. Polym. Sci.* **1983**, *28*, 3453−3466.
(11) Bersted, B. H.; Lee, J. D.; Richter, C. A. *J. Appl. Polym. Sci.* **1981**, *26*, 1001−1014.
(12) Hughes, J. K. *SPE Antec Technol. Papers* **1983**, *29*, 306−309.
(13) Vega, J. F.; Santamaria, A.; Munoz-Escalona, A.; Lafuente, P. *Macromolecules* **1998**, *31*, 3639−3647
(14) Mavridis, H.; Shroff, R. *J. Appl. Polym. Sci.* **1993**, *49*, 299−318.
(15) Lai, S.; Plumley, T. A.; Butler, T. I.; Knight, G. W.; Kao, C. I. *SPE Antec Technol. Papers* **1994**, 40, 1814−1815.

(16) Shroff, R.; Mavridis, H. *J. Appl. Polym. Sci.* **1995**, *57*, 1605−1626.
(17) Wasserman, S. H.; Graessley, W. W. *Polym. Eng. Sci.* **1996**, *36*, 852−861.
(18) Wasserman, S. H. *"Metallocene-Catalyzed Polymers", Plastics Design Library-SPE*; SPE: New York, 1998; pp 185−192.
(19) Sakai, T. *J. Polym. Sci., A2* **1968**, *6*, 1659−1672.
(20) Sabia, R. *J. Appl. Polym. Sci.* **1963**, *7*, 347.
(21) Graessley, W. W.; Raju, V. R. J. *Polym. Sci., Polym. Symp.* **1984**, *71*, 77−93.
(22) Raju, V. R.; Smith, G. G.; Marin, G.; Knox, J. R.; Graessley, W. W. *J. Polym. Sci.* **1979**, *17*, 1183−95.
(23) Shroff, R. N. U.S. Patent 5,486,575, Jan. 23, 1996.
(24) Graessley, W. W. *Adv. Polym. Sci.* **1974**, *17*, 70−71.
(25) Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301−1314.
(26) Scholte, Th. G. Characterization of Long-Chain Branching in Polymers. In *Developments in Polymer Characterization-4*; Dawkins, J. V., Ed.; Applied Science Publishers: Oxford, England, 1993.
(27) Meissner, J. *J. Pure Appl. Chem.* **1975**, *42*, 553−612.
(28) Porter, R. S.; Johnson; J. F. *J. Polym. Sci.* **1966**, *C15*, 373−380.
(29) Vinogradov, G. V.; Ya Malkin, A. *Rheology of Polymers*; Springer-Verlag: New York, 1980; Chapter 2.
(30) Verser, D. W.; Maxwell, B. *Polym. Eng. Sci.* **1970**, *10*, 122−130.
(31) Mavridis, H.; Shroff, R. *Polym. Eng. Sci.* **1992**, 32, 1778−1791.
(32) Cogswell, F. N. *Polym. Eng. Sci.* **1972**, *12*, 64−73.
(33) Shroff, R. N.; Cancio, L. V.; Shida, M. *Trans. Soc. Rheol.* **1977**, 21: 3, 429−466.
(34) Ramkummar, D.; Caruthers, J.; Mavridis, H.; Shroff, R. *J. Appl. Polym. Sci.* **1997**, *64*, 2177−2189.
(35) Shroff, R.; Prasad, A.; Lee, C. *J. Polym. Sci.* **1966**, *B34*, 2317−2333.
(36) Drott, E. E.; Mendelson, R. A. *J. Polym. Sci., A-2* **1970,** *8*, 1361−1371.
(37) Drott, E. E.; Mendelson, R. A. *J. Polym. Sci., A-2* **1970**, *8*, 1373−1385.
(38) Mirabella, F. M., Jr.; Wild, L. In *Polymer Characterization: Physical Property, Spectroscopic and Chromatographic Methods*; Craver, C. D., Provder, T., Eds.; Advances in Chemistry Series 227;American Chemical Society: Washington, DC, 1990.
(39) Nakajima, N.; Wong, P. S. L. *Trans. Soc. Rheol.* **1965**, *9* (1), 3−11.
(40) Shida, M.; Cote, J. A. *Preprints International Symposium on Macromolecular Chemistry (Toronto)*; IUPAC: 1968; pp A8.14−A8.18.
(41) Graessley, W. W. *J. Chem. Phys.* **1967**, 47, 1942−1953.
(42) Shida, M.; Cancio, L. V. *Polym. Eng. Sci.***1971**, *11* (2), 124−128.
(43) Plumley, T. A.; Lai, S. Y.; Betso, S. R.; Knight, G. W. *SPE Antec Technol. Pap.* **1994**, *40* (1), 1221−1225.
(44) Wild, R.; Ranganath, R.; Knobeloch, D. C. *Polym. Eng. Sci.* **1976**, 16, 811−813.
(45) Yasuda, K.; Armstrong, R. C.; Cohen, R. E. *Rheol. Acta* **1981**, *20*, 163−178.

MA9909354