Detection of Low Levels of Long-Chain Branching in Polydisperse Polyethylene Materials

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ABSTRACT: Creep experiments have been applied to probe the zero-shear viscosity, η_0, of polyethylene chains directly and precisely in a constant-stress rheometer at 190°C. Such experiments, when combined with precise measurements of the weight-average molecular weight, M_w, calibrated relative to linear chains of high-density polyethylene, are shown to provide a very sensitive approach to detect low levels (0.005 branches per 1000 carbons) of long-chain branching (LCB). This detection limit is shown to be insensitive to whether the molecular weight distribution (MWD) breadth, M_w/M_n, rises from about two to ten. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 636–646, 2011

Key words: polyethylene; long-chain branching; zero-shear viscosity; molecular weight distribution

INTRODUCTION

Thermoplastic materials are commonly fabricated into films, fibers, bottles, foams, or molded parts by flow in the molten state. A key innovation in the fabrication of molten thermoplastics was the introduction of low levels of branched chains. There are many classes of branched chains available to thermoplastics. Of interest here are chains with long-chain branching (LCB). Materials with LCB contain chains with branches that are considered "rheologically long"; this means that the molecular weight of any straight-chain branch exceeds the chain entanglement molecular weight, M_e, so that the entangled branch can elevate the viscosity of the molten chains when subjected to creeping flows. Additionally, the branched chains of interest here contain only a few branch sites/chain, and their concentration in a mixture of linear and branched chains should be sufficiently dilute that the low-shear-rate viscosity in the molten state rises as the concentration of branched chains increases. Often, the branching frequency of such materials is low, and typically less than about 0.1 LCB/1000 carbons.

The impact of LCB is especially important in polyethylene materials due to their low entanglement molecular weights ($M_e = 1200$ g/mol, 190°C).[1] These materials have been used to enable: (1) easy flow at rapid fabrication rates due to an enhanced ability to shear thin, (2) faster fabrication rates due to an ability to delay the onset of surface and/or gross melt fracture,[2,3] (3) films to be blown with higher stability due to enhanced strain hardening, and (4) lower-density foams to be fabricated due to an enhanced ability to be stretched to higher break strains/stresses. An ability to detect and control low levels of LCB is key to accelerating the design of these high-performance materials.

Complementary methods to detect LCB involve rheology of molten undiluted chains,[4] [13]C nuclear magnetic resonance (NMR) of semi-dilute chains,[5,6] and/or triple-detector gel permeation chromatography (TD-GPC) of very dilute chains.[7] The ^{13}C-NMR experiment[5] is straightforward to interpret; it weights all branches greater than a hexyl branch the same regardless of the branch length and reports a branching frequency value in units of branches/1000 carbons. A recent study by Parkinson et al.[6] found a systematic change in the ^{13}C spin-lattice relaxation time (T_1^c) of the terminal branch carbons when the branch length is between 6 and 16 carbons from solid-state NMR measurements. However, such an approach still can not differentiate among the branches that are just longer than 16 carbons relative

to rheologically-long branches. In TD-GPC the LCB metrics are derived from the simultaneous dilute-solution determinations of the concentration, the intrinsic viscosity, and the molecular weight of various polymer fractions eluted as a function of hydrodynamic volume, followed by a detailed comparative analysis of two sets of such fractions obtained, respectively, from linear and branched polymers (as represented in the Mark-Houwink plots).[7] The rheology of molten undiluted chains, and the focus of this study, is used for the detection of rheologically-long branches.

Shear rheology of molten undiluted chains is often preferred to detect low levels of LCB. This is because only a few long side chains are needed to drastically change the relaxation behavior of the entangled chains.[8] Studies[9,10] have also found that the longest relaxation time of any LCB chain has a strong exponential dependence on the length of the side chains, but a relatively weak dependence on the branching frequency. Such changes in the rheological responses have been utilized in detecting levels of LCB in polymers by several different approaches.[11] For example, by measuring the level of the plateau in the plot of loss angle versus angular frequency,[12] or via the plot of loss angle versus complex modulus (the so-called "van Gurp-Palmen plot").[13] Another commonly-used method is based on zero-shear viscosity, η_0, and weight-average molecular weight, M_w, data. Materials[14] with η_0 exceeding that expected for linear chains with the same M_w were considered to contain sparse levels of long-chain branches. The power-law dependence, as shown in eq. (1), has been established for many types of polymers when they are molten, homogeneous (single phase), and solely composed of long linear chains. Typically, the exponent α varies between 3.4 and 3.6, and the κ values are generally dependent on the polymer species.[15,16]

$$\eta_0 = \kappa\, M_w^{\alpha} \tag{1}$$

There are challenges in establishing such a relationship as in eq. (1) for linear-chain polyethylene materials. The power-law relationships established for other polymers are mostly based on nearly monodisperse samples. However, it is challenging to obtain polyethylene with very narrow molecular weight distribution (MWD), except through tedious fractionation. Although nearly monodisperse polyethylenes have been successfully produced by hydrogenation of ionic-polymerized polybutadienes,[17] short chain branching resulting from 1,2-polybutadiene still can not be completely excluded. Another challenge is the molecular weight range of the samples, since a robust relationship should be established based on a wide range of molecular weights. The effect of comonomer type and level, and the accuracy and precision of the reported data, including both η_0 and M_w values, are critical. Finally, the effect of the MWD on the power-law relationship is yet another challenge, which is the focus of this study.

There have been several studies on η_0 and M_w relationships for polyethylene. As previously noted, a power-law exponent of 3.4–3.6 has generally been observed for linear polyethylene.[18–22] In studies in which the exponents exceed the traditional range (α = 3.4–3.6), the polymers have often been suspected to contain low levels of LCB. The article by Raju et al.[14] is the most often quoted article in this area. Fractionated polyethylene samples with narrow MWD ($M_w/M_n < 1.2$) were used to develop a correlation for linear-chain materials with α = 3.60. Wood-Adams et al.[7] confirmed the η_0/M_w relationship for linear-chain metallocene polyethylenes. Gabriel et al.[22] showed this method could be used with narrow MWD metallocene samples to show LCB in samples as low as 0.03 LCB/1000C as determined by ^{13}C-NMR. Malmberg et al.[23] also examined the effect of metallocene materials made with comonomer on this relationship, although the comonomer content and LCB content were not directly measured.

Raju et al.[14] reported that two polyethylene materials (M_w = 149,000 g/mol and 520,000 g/mol) had η_0 exceeding those expected for linear-chain materials with the same M_w, and presumed such materials were branched even though they were prepared under conditions thought to solely produce linear chains. In contrast, others anticipate that at higher molecular weights,[24] there will be elevated values of α. Porter and Johnson[25] quoted an elevated exponent of α = 6–8 for higher molecular weight materials. Gabriel and Munstedt[26] also found a reported linear HDPE (M_w = 284,000 g/mol) which did not follow the power-law relationship established for linear chains. It has also been noted that as the molecular weight increases[27,28] there is a greater deviation from the linear-chain power-law relationship. Metallocene-catalyzed materials were found to have an α = 4.2 which was inferred[29] to result from LCB. A model[24] was developed to predict zero-shear viscosities and branching statistics. It was noted that there was a greater deviation from the linear-chain power-law relationship for a given LCB level at higher molecular weights.[27,28] At LCB levels exceeding about 0.1 LCB/1000C, it is predicted that with increasing LCB levels, the viscosity will drop at a given molecular weight with the hypothesis that at high levels of LCB the average length of the LCB would be less, resulting in shorter relaxation times. In addition, very high levels of LCB could potentially inhibit inter-chain entanglements. The comonomer type and level have been reported[7,30,31] to not affect the relationship between η_0 and M_w for linear chains.

TABLE I
Selected Properties of the High-Density Polyethylene Materials

Resin	Density ρ (g/cm^3)	Melt index I_2 (dg/min)	NMR LCB/1000C	GPC M_n (g/mol)	GPC M_w (g/mol)	GPC M_w/M_n	LALLS M_w (g/mol)	η_0 (dynamic) (Pa•s) 190°C	η_0 (creep) (Pa•s) 190°C
HD1	n/m	n/m	0	13,700	27,800	2.04	25,400	37	38.4
HD2	n/m	n/m	0	37,700	75,500	2.00	70,500	1500	1530
HD3	0.953	0.97	0	43,800	121,000	2.75	115,000	8050	8010
HD4	n/m	n/m	0	65,500	139,000	2.13	133,000	15,200	14,800
HD5	n/m	n/m	0	78,800	158,000	2.01	150,000	n/m	20,900
HDS1	n/m	620 cp*	0	2800	7800	2.79	n/m	0.414	n/m
HDS2	n/m	850 cp*	0	2990	8540	2.86	n/m	0.586	n/m
HDS3	n/m	1940 cp*	0	4160	11,400	2.74	n/m	1.30	n/m
HDS4	n/m	5480 cp*	0	5330	14,800	2.78	n/m	3.78	n/m
HDS5	n/m	145	0	12,300	28,300	2.30	n/m	63.7	56.9
HDS6	0.953	0.83	0	59,600	121,000	2.03	114,000	n/m	9480
HDS7	n/m	n/m	0	92,200	221,000	2.40	220,000	n/m	74,300
HDS8	0.951	n/m	0	47,500	449,000	9.45	n/m	n/m	no s.s.#
HDS9	0.930	n/m	0	230,000	980,000	4.26	n/m	n/m	no s.s.#
HDB8	0.956	1.10	0.020	52,200	111,000	2.12	104,000	7990	8040
HDB9	n/m	0.26	0.023	70,600	160,000	2.27	150,000	37,700	54,100
HDB10	0.956	0.84	0.190	32,400	69,500	2.15	n/m	n/m	18,400

For four samples (*), the Brookfield melt viscosity at 177°C (1 cp = 1 mPa s) was measured instead of melt index. Two samples (#) did not achieve steady state in the creep test.

Several studies have reported no effect of a broad MWD on the power-law relationship for linear-chain materials.[14,29,32,33] However, Hatzikiriakos[34] and Saeda et al.,[35] both reported an effect of MWD on the power-law relationship resulting in an increase in the power-law exponent α. From the work of Saeda et al.,[35] the exponent changed from α = 3.42–3.97 as M_w/M_n varied from 1.2 to 19. In both cases, melt viscosities, η_0, for these broader-molecular-weight distribution materials exceeded those of narrower MWD samples for any given M_w. Similarly, viscosities of commercial polyethylenes with bi-modal MWDs were also shown to exceed those of narrow-molecular-weight-distribution samples.[36]

Work by this group has focused on the use of types of shear rheology able to fingerprint the full spectrum of relaxation of the undiluted molten chains. Creep experiments are preferred to probe the longer relaxation times associated with motions of high molecular weight linear and non-linear chains. These experiments are done with very precise and direct approaches with the relaxation spectrum summarized in terms of the zero-shear viscosity, η_0. In addition, this group uses both conventional GPC and low-angle laser light scattering (LALLS) data to provide very precise measurements of the weight-average molecular weight, M_w. Conventional GPC data are preferred over LALLS data to enhance the contrast between linear and branched materials with the same M_w. Additionally, and out of the scope of this article, we find that conventional GPC data are also preferred, relative to LALLS data,[31] to interpret low LCB levels in ethylene α-olefin copolymers.[37]

The advantage of the conventional GPC method is that it is dominated by the "backbone" molecular weight of the homopolymer linear and branched chains.[38,39]

Extensive sets of model materials were prepared to examine the effect of the breadth of the molecular-weight-distribution on the ability to detect low levels of LCB in polyethylene materials.[37,40] All materials are based on innovative metallocene catalysts,[2,3,41,42] which are known for their ability to produce polyethylene chains with well-defined structures and reduced polydispersities. Such materials, of course, were not available for many of the studies previously discussed in the literature. Overall, these results provide an unprecedented and definitive view of the impact of MWD on the detection of low LCB levels in polyethylene materials.

EXPERIMENTAL

Materials

The materials discussed in this work are summarized in Table I, in which "HD" refers to high density polyethylene (HDPE), "HDS" refers to a supplemental set of HDPE, and "HDB" refers to a high density set of samples with LCB. HD1, HD2, and HD4 are polyethylene homopolymers produced in a batch reactor with a constrained geometry catalyst (Titanium, [N-(1,1-dimethylethyl)-1,1-dimethyl-1-[(1,2,3,4,5-η)-2,3,4,5-tetramethyl-2,4-cyclopentadien-1-yl]sila-naminato(2-)-κN]dimethyl-) at low conversion to avoid LCB formation. Sample HD3 is a polyethylene

TABLE II
Selected Properties of the High-Density Polyethylene Blends

Resin	Density ρ (g/cm^3)	Melt index I_2 (dg/min)	NMR LCB /1000C	GPC M_n (g/mol)	GPC M_w (g/mol)	GPC M_w/M_n	LALLS M_w (g/mol)	η_0 (creep) (Pa•s) 190°C
B0P2	0.953	0.83	0	59,600	121,000	2.03	114,000	9570
B1P2	0.954	0.74	0.005	57,700	122,000	2.11	116,000	13,700
B2P2	0.954	0.69	0.010	55,500	120,000	2.17	115,000	13,700
B3P2	0.957	0.99	0.056	39,400	102,000	2.58	94,600	10,600
B4P2	0.957	0.82	0.109	40,200	87,800	2.18	80,800	16,000
B0P4	0.960	1.40	0	29,500	122,000	4.14	114,000	10,800
B1P4	0.961	1.08	0.014	25,100	112,000	4.47	102,000	11,000
B2P4	0.959	0.81	0.052	26,500	105,000	3.96	98,700	15,600
B3P4	0.959	0.85	0.106	22,500	85,800	3.81	99,400	17,200
B0P6	0.963	1.66	0	18,800	127,000	6.75	129,000	9600
B1P6	0.962	1.15	0.013	16,800	102,000	6.09	96,800	10,000
B2P6	0.961	0.86	0.052	16,100	103,000	6.37	94,200	14,200
B3P6	0.960	1.16	0.106	15,000	83,200	5.55	77,200	11,500
B0P8	0.965	2.86	0	15,200	131,000	8.64	133,000	9840
B1P8	0.963	1.17	0.014	11,800	104,000	8.85	94,400	10,100
B2P8	0.962	0.87	0.052	12,300	101,000	8.20	93,500	14,300
B0P10	0.967	3.31	0	11,900	131,000	11.0	135,000	10,900
B1P10	0.966	1.15	0.014	10,200	102,000	10.0	96,900	9920
B2P10	0.963	0.91	0.070	9230	93,400	10.1	88,300	12,500

The NMR values of LCB/1000C were computed based on the weight fraction w_i and NMR LCB/1000C[i] values measured for blend component i.

homopolymer produced using the same catalyst on a silica support. This material was used in powder form to eliminate any processing history which may have occurred upon pelletization. HD5 is a polyethylene homopolymer produced in a batch reactor using a zirconocene dichloride catalyst. This set of polyethylene homopolymers (HD1 - HD5) was selected as linear-chain reference materials. This set represents a wide range of molecular weights (25,000 g/mol $< M_w <$ 160,000 g/mol), and all have low polydispersities ($2 < M_w/M_n < 3$).

The antioxidant level in each of the linear-chain samples was determined via infrared spectroscopy. If the antioxidant level was low, antioxidant was added to achieve the recommended levels of 2000 ppm total antioxidant, with a 2 : 1 ratio of Irgafos 168 to Irganox 1010 (Trademark of Ciba Specialty Chemicals); (1333 ppm Irgafos 168 and 667 ppm Irganox 1010).

A supplemental set of linear-chain polyethylene homopolymers (HDS1, HDS2, … HDS9) was identified to augment the HD set at lower and higher M_w. These samples extended the molecular weight range to (7,800 g/mol $< M_w <$ 980,000 g/mol) and were used as blend components to produce samples of broader MWD. A final set of polyethylene homopolymers (HDB8, HDB9, HDB10) contained low levels of branched chains, ranging from about 0.02 to 0.2 LCB/1000C as determined from NMR studies.

All, but two materials, were produced by solution polymerization[2,3] on the miniplant scale; two materials (HDS8 and HDS9) were produced by slurry polymerization on the miniplant scale. The general

method of producing these samples is described elsewhere.[2,3]

A set of 19 blends was prepared with the HDS and HDB materials. The blends were designed to have target LCB levels (LCB/1000C $\approx$ 0, 0.005, 0.01, 0.05, and 0.1) and molecular-weight-distribution breadths ($M_w/M_n \approx$ 2, 4, 6, 8, and 10). The blends were denoted as BnPm with integer index n indicating the branching level and integer index m set to the target M_w/M_n. The blends were prepared in an extruder to deliver materials with target M_w/M_n and LCB values. Mild conditions (250-rpm screw speed, 120–190°C, nitrogen purge) were selected to minimize changes in the polymers due to possible structure changes (e.g., chain scission, crosslinking, etc.), and the extrudate was quenched into chilled water, air dried, and pelletized. Selected properties of the blends are found in Table II.

Blend design

The components and weight fractions selected to prepare each blend were determined by simulations of ideal MWDs using simple curve fitting routines. The curve fitting was based on the MWD measured by GPC for each blend component (with and without LCB), and combined to closely approximate the GPC log-normal probability distribution target. The simulated solutions for each blend were obtained by adding these components as weighted fractions to achieve the overall log-normal distribution shape, the desired LCB level, the desired weight-average molecular weight,

TABLE III
Weight Fraction of Components in the High-Density Polyethylene Blends

Resin	w_{HDS1}	w_{HDS2}	w_{HDS3}	w_{HDS4}	w_{HDS5}	w_{HDS6}	w_{HDS8}	w_{HDS9}	w_{HDB8}	w_{HDB9}	w_{HDB10}
B0P2	–	–	–	–	–	1.0000	–	–	–	–	–
B1P2	–	–	–	–	–	0.9737	–	–	–	–	0.0263
B2P2	–	–	–	–	–	0.9474	–	–	–	–	0.0526
B3P2	–	–	–	–	–	–	–	–	0.7895	–	0.2105
B4P2	–	–	–	–	–	–	–	–	0.4737	–	0.5263
B0P4	–	–	–	–	0.3110	0.6540	0.0210	0.0140	–	–	–
B1P4	–	–	–	–	0.3850	–	–	–	–	0.6150	–
B2P4	–	–	–	0.0196	0.2556	–	–	–	–	0.5144	0.2105
B3P4	–	–	–	0.1170	0.0420	–	–	–	–	0.2520	0.5880
B0P6	–	–	–	0.0680	0.4000	0.4680	0.0390	0.0250	–	–	–
B1P6	0.0133	0.0062	0.0027	0.0940	0.2987	–	–	–	–	0.5851	–
B2P6	0.0006	0.0003	0.0939	0.0652	0.1076	–	–	–	–	0.5220	0.2105
B3P6	0.0620	0.0040	0.0420	0.0970	–	–	–	–	–	0.2690	0.5260
B0P8	–	–	0.1410	0.0010	0.3690	0.4140	0.0460	0.0290	–	–	–
B1P8	0.0936	0.0276	0.0001	0.0313	0.2565	–	–	–	–	0.5909	–
B2P8	0.0265	0.0538	0.0601	0.1207	–	–	–	–	–	0.5283	0.2105
B0P10	–	–	0.2450	–	0.2950	0.3770	0.0510	0.0320	–	–	–
B1P10	0.1540	0.0169	0.0046	0.0790	0.1448	–	–	–	–	0.6006	–
B2P10	0.1918	0.0300	0.0047	0.0155	–	–	–	–	–	0.4422	0.3158

and the desired polydispersity (or equivalently the targeted number average molecular weight).

The linear-chain blends (B0P2, B0P4 B0P6, B0P8, and B0P10) in Table II were designed with the linear-chain components (HDS1–HDS6; HDS8 and HDS9). The target M_w was selected to be that (121,000 g/mol) measured for the HDS6 material. The blends with branched chains were similarly designed but with different components (HDS1–HDS5; HDB8, HDB9, and HDB10). The target for M_w was relaxed somewhat in favor of achieving the best fit to the targeted distribution and also achieving the desired overall LCB level. The process used to prepare the blends met most of the targets as seen from their measured M_w and M_w/M_n values reported in Table II. The weight fractions of the components for the blends are reported in Table III.

Properties

Densities were measured at room temperature by ASTM D-792. The melt index I_2 was measured at 190°C by ASTM D-1238. Branching levels (long branches/1000 carbons) were measured by ^{13}C-NMR for the blend components.[5,7] Blend branching levels were computed from the LCB/1000C[i] and weight fraction, w_i, of all components ($i = 1, 2, 3, \ldots$) based on the method of standard addition.[43]

$$\frac{LCB}{1000C}[\text{blend}] \approx \sum_i w_i \frac{LCB}{1000C}[i] \qquad (2)$$

Molecular weight

Both GPC and LALLS were used to determine molecular weights. For the GPC measurements, the chromatographic system consisted of either a Polymer Laboratories (a wholly owned subsidiary of Varian, Palo Alto, CA) Model PL-210 or a Polymer Laboratories Model PL-220. The column and carousel compartments were operated at 140°C. Three Polymer Laboratories 10-μm Mixed-B columns were used with a solvent of 1,2,4-trichlorobenzene. The samples were prepared at a concentration of 0.1 g of polymer in 50 mL of solvent. The solvent used to prepare the samples contained 200 ppm of the antioxidant butylated hydroxytoluene (BHT). Samples were prepared by agitating lightly for two hours at 160°C. The injection volume used was 100 microliters, and the flow rate was 1.0 mL/min. Calibration of the GPC column set was performed with narrow MWD polystyrene standards purchased from Polymer Laboratories. The polystyrene standard peak molecular weights were converted to polyethylene molecular weights using:[44]

$$M_{\text{polyethylene}} = A(M_{\text{polystyrene}})^B \qquad (3)$$

in which, M is the molecular weight, A has a value of 0.4316, and B is equal to 1.0. Polyethylene equivalent molecular weight calculations were performed using Viscotek TriSEC software Version 3.0. The precision of the weight-average molecular weight $\Delta M_{w,2s}$ was excellent at <2.6%.

Absolute molecular weights were determined by LALLS on a Polymer Laboratories PL210 high-temperature GPC equipped with a Viscotek (Houston, TX) model 210R viscometer and a Precision Detectors (Franklin, MA) PD2000 light scattering detector.[7] All conditions were the same as with the GPC. The system was calibrated using a standard polyethylene material (NBS 1475) with a weight-average molecular weight of

M_w = 52,000 g/mol and an intrinsic viscosity of $[\eta]$ = 1.01 dL/g. The mean and standard deviations, based on at least four replicate studies, were reported for the intrinsic viscosity, $[\eta]$, and the weight-average molecular weight, M_w. The precision of the LALLS weight-average molecular weight $\Delta M_{w,2s}$ was very good at <2.4%.

Shear rheology

Creep experiments were measured in nitrogen at 190°C in a constant-stress rheometer (SR 5000 or DSR500, TA Instruments (New Castle, DE)) with parallel-plate fixtures (25-mm-diameter, stainless steel, ~ 1.5-mm gap). Data points were collected at equal time intervals for selected durations between about 2,000 and 160,000 s. The shear creep compliance, $J(t,\sigma) \equiv \gamma(t)/\sigma$, was computed for each point from the strain, $\gamma(t)$, measured from the rest state after application of a constant stress, σ. Steady-state flow (e.g., $d\ln J(t,\sigma)/d\ln t \geq 0.99$) was observed at long creep times, t, and the $J(t,\sigma)$ data were fit to a simple linear dependence $[J(t,\sigma) = J(\sigma) + t/\eta]$ with 10–30 points to determine the steady-state viscosity, η. Moreover, at very low applied shear stress, σ (e.g., 10–50 Pa), the shear creep compliance data were insensitive to σ, allowing η measured at 20 Pa to be also identified as the zero-shear viscosity, η_0. This approach is direct in the sense that no extrapolations to steady state or zero shear rate are needed. Values reported for η_0 are means of a set of replicate studies with each replicate based on a fresh sample. The precision, $\Delta\eta_{0,2s}$, of the zero-shear viscosity was ≤2%.

The superposition of oscillatory shear flow viscosity data (100–0.1 rad/s, 5 points/decade, amplitudes in the linear viscoelastic regime) measured just before and just after the creep experiments were used to verify the stability of the molten materials during the creep studies. These oscillatory shear flow experiments were also key to determine the zero-shear viscosity for the lowest-molecular-weight materials (M_w < 30,000 g/mol; HDS1, HDS2, HDS3, HDS4, HDS5). The dependencies of the magnitude $|\eta(\omega)|$ of the complex viscosity for these five materials were nearly insensitive to the angular oscillation frequency, ω, at low ω, and the data could be fit straightforwardly with non-linear regressions to several simple models to identify the zero-shear viscosity, η_0. The results for η_0 were model independent; only values from the Cross model $\{|\eta(\omega)| = \eta_0 [1 + (\omega\tau)^{1-n}]^{-1}\}$ are reported.

RESULTS AND DISCUSSION

Linear-chain materials

The MWDs for the HD1–HD5 set of high-density polyethylene materials were monomodal as shown
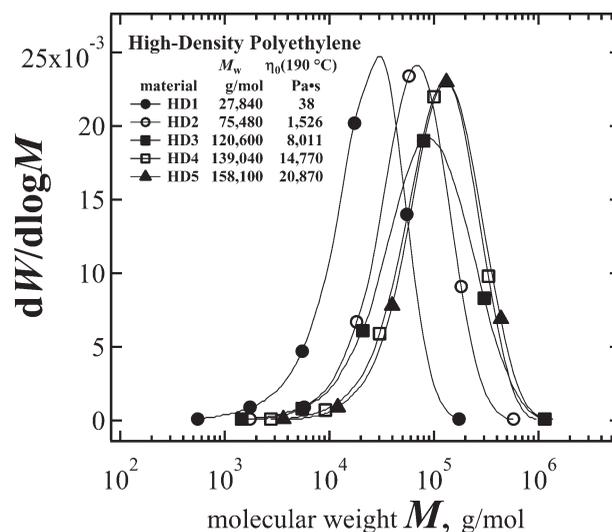
Figure 1 Molecular weight distributions for high-density polyethylene materials (HDS1–HDS5).

in Figure 1. The distributions are constructed with straight-line segments between the adjacent points; distinct symbols for each material are added to selected points on each distribution. Two moments of their distributions are found in Table I.

The MWDs of the high-density polyethylene materials used to produce the blends are shown in Figure 2(a,b). The levels of LCB/1000C probed by NMR studies are reported in Table I; only the HDB materials contain nonlinear (branched) chains. All distributions are found to be monomodal. The materials prepared by solution polymerization have symmetric distributions and similar distribution breadths (M_w/M_n = 2–3). The two materials prepared by slurry polymerization (HDS8 and HDS9) have nonsymmetric distributions, broader distribution breadths (M_w/M_n = 4.3–9.5), and the highest values of M_w.

Typical creep data for selected linear-chain materials are shown in Figure 3. The data are displayed with straight-line segments between the adjacent points; distinct symbols for each material are added to selected points on each curve. Data at long times have reached steady-state flow since their slopes, $d\ln J(t,20 \text{ Pa})/d\ln t$, are nearly unity (broken-line curves at long times are drawn with slopes of unity). Values of η_0 measured by creep experiments are summarized in Tables I and II.

Oscillatory shear flow experiments were used to obtain η_0 for five low-viscosity materials (HDS1, HDS2, HDS3, HDS4, HDS5). The results are displayed in Figure 4. The dependence of the magnitude of the complex viscosity, $|\eta^*|$, on angular frequency, ω, is weak for these low-viscosity materials. A nonlinear regression was used to fit the data (discrete points) with a three-parameter Cross model
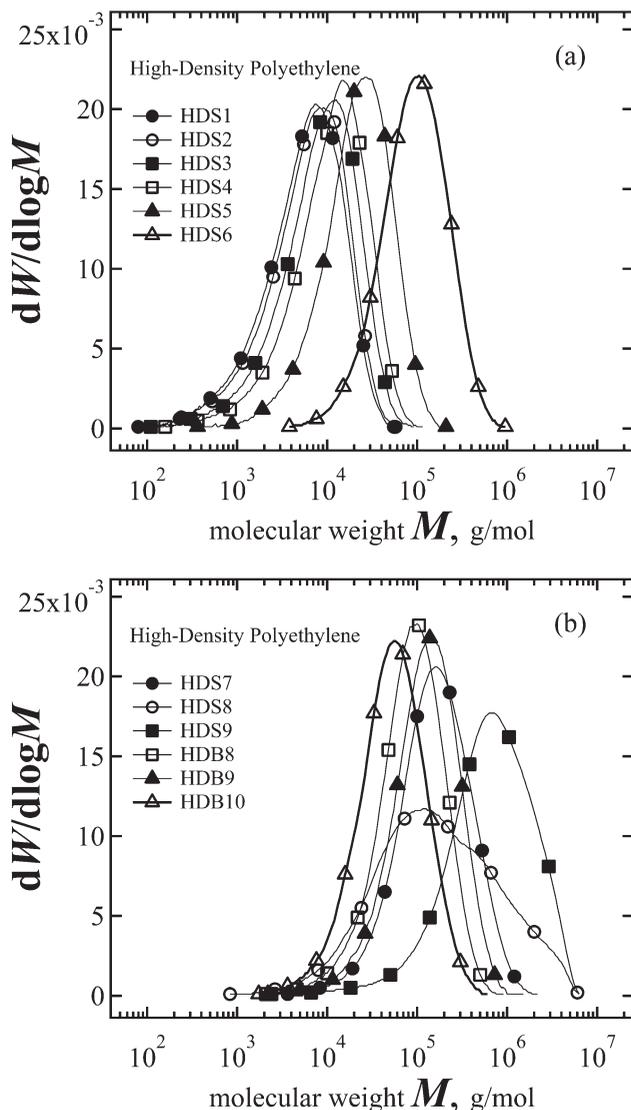
Figure 2 Molecular weight distributions of the high-density polyethylene reference materials used to produce blends. Included are (a) samples HDS1–HDS6 and (b) HDS7–HDS9 and HDB8–HDB10.

$(|\eta^*| = \eta_0 [1 + (\omega\tau)^{1-n}]^{-1})$. The fits were excellent, and are shown with broken line curves. Only one fit parameter, η_0, is summarized in Table I. When the predicted complex viscosities from the Cross model are compared to the actual measured values, the correlation coefficient R^2 ranges from 0.99 to 0.69 with the higher molecular weight or higher viscosity samples generally showing the best fit.

The power-law relation between η_0 and M_w is illustrated in Figure 5. The regression fit to the data for the HD set (open circles) is illustrated with the solid line of eq. (1) in which $\kappa = 2.29 \times 10^{-15}$ and $\alpha = 3.65 \pm 0.08$ (two standard deviations), in which η_o is in Pa•s and M_w is in g/mol. The reported error and associated confidence intervals apply strictly to the linear regression relating the η_0 and GPC M_w for the five HD materials. Also shown in Figure 5 are
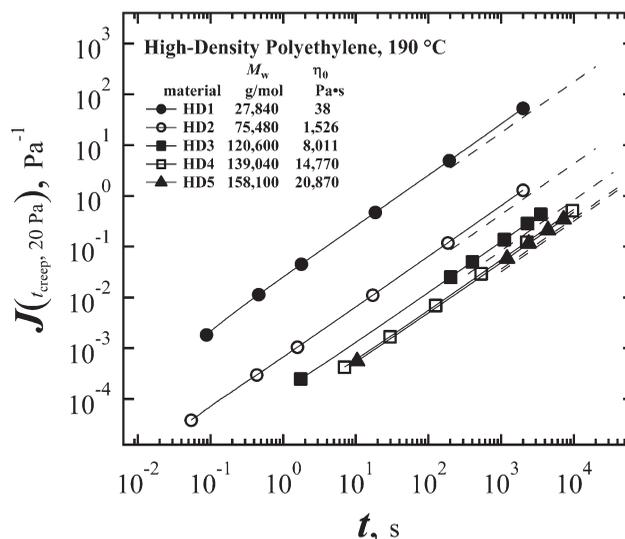
Figure 3 Dependency of the creep compliance, J $(t, 20$ Pa), on creep time, t, for selected high-density polyethylene materials at 190°C.

the 95% confidence limits (dashed-line) for the regression fit to these materials; these limits are used to guide the interpretation of the presence of low LCB levels since data measured for materials with LCB levels exceeding about 0.005 LCB/1000C often far exceed the upper confidence limit. The reported range of the 95% confidence interval depicted in Figure 5 was limited by a number of factors, but primarily the precision of each of the methods was of overriding importance. The observed relative standard deviation (RSD) for the determination of the weight-average molecular weight (g/mol) using the GPC method was 1.3% ($n = 5$), which was nearly the same as for the LALLS method (1.2%, $n = 10$).
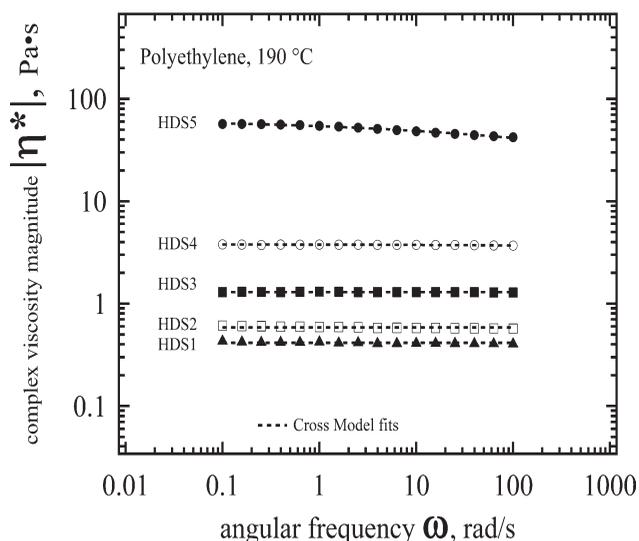
Figure 4 Dependency of the magnitude $|\eta^*|$ of the complex viscosity at 190°C on angular frequency, ω, for selected HDS materials.
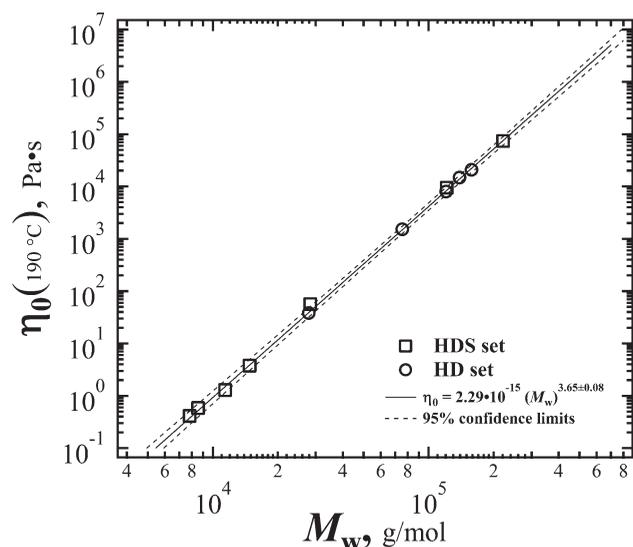
Figure 5 Dependency of the zero-shear viscosity, η_0, at 190°C on the weight-average molecular weight, M_w, for the HD and HDS high-density polyethylene materials.

Similarly, the observed precision for the creep determination (Pa•s) in terms of RSD was 1.5% ($n = 3$). In the calculation of the regression confidence interval, the averaged data (with $n = 5$ ordered pairs) were employed and all the errors are assigned to η_0. The full regression step would ideally be repeated in response to any changes in GPC column calibrations or operating conditions if one were trying to achieve the best repeatability for a particular determination.

It is important to emphasize a key point about the use of the conventional GPC M_w, rather than the LALLS M_w, to detect low LCB levels in this method. Choosing the GPC M_w values over those provided by LALLS maximizes the apparent deviation or distance between those η_0 and M_w data points measured for materials with LCB and the power-law relationship derived from a set of linear-chain materials (without LCB). This maximizes the sensitivity of the η_0 and M_w method. This feature adds to the robustness of the η_0 and M_w method to detect low LCB in ethylene polymers.

This power-law relationship for the linear-chain materials shown in Figure 5 is experimentally indistinguishable from that reported by Raju et al.[14] for fractionated high-density polyethylene. The experimental M_w window for the fit covers a range from about 25,000 to 160,000 g/mol. The open squares in Figure 5 denote data for the HDS set of materials, which were used as blend components. Results for six of the HDS materials fall within the 95% confidence limits of the regression fit, and independently confirm the NMR analysis that they are solely composed of linear chains. Four of these linear-chain materials (HDS1, HDS2, HDS3, and HDS4) have

much lower M_w than those of the HD set of linear-chain reference materials and demonstrate that the power-law relationship for linear chains is valid to M_w as low as 7,800 g/mol. This result validates the LCB analysis with M_w and η_0 data to lower M_w. Differences in the power-law fit coefficients, relative to those of others[18,25,30,35,23] using such low M_w materials, are assumed to be due primarily to updated approaches to measure and calibrate M_w and η_0. The M_w (7,800 g/mol) for the HDS1 is evidently very close to the estimated critical molecular weight M_c (2.700 ± 1,000 g/mol)[13,39–41,45–47] for polyethylene.

Results for one blend component material fall slightly above the 95% confidence limits for the power-law fit to the data for linear-chain materials. This material (HDS5, $M_w = 28,300$ g/mol) is thought to be solely composed of linear chains based on its synthesis even though its η_0 exceeds the 95% confidence limit by 9%. The point re-enforces our use of confidence limits as guidelines to interpret branching levels, since 5% of the results for linear-chain materials should exceed these 95% confidence limits. This issue will not interfere with our interpretation of materials with low LCB levels, since data for these LCB materials will much more strongly exceed these 95% confidence limits.

Impact of Molecular Weight Distribution

The impact of MWD on the η_0 and M_w relationship is shown in Figure 6. The results are shown in a similar way as those in Figure 5, but the x- and y-axis scales are greatly magnified and focused on the high M_w regime. Results for four of the five blend
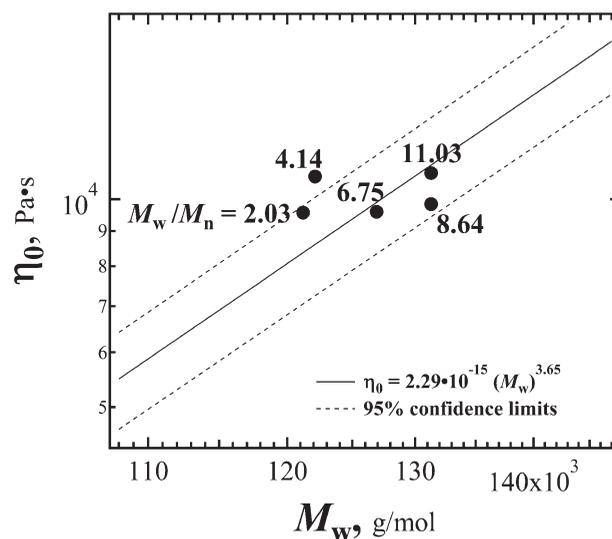
Figure 6 Dependency of the zero-shear viscosity, η_0, at 190°C on the weight-average molecular weight, M_w, for the high-density polyethylenes with varying molecular weight distribution.

materials (B0P2, B0P6, B0P8, B0P10) prepared from linear-chain components fall within the 95% confidence limits. These materials are consequently confirmed to be solely composed of linear chains. This result is strong evidence that the components did not contain branched chains, as well as, that the blending process did not create branched chains. This result also demonstrates the insensitivity of the power-law relationship between M_w and η_0 to the molecular-weight-distribution breadth as measured by the polydispersity range of the samples ($2 < M_w/M_n < 10$).

The η_0 of one material (B0P4, $M_w = 122{,}100$ g/mol) exceeds the 95% confidence limit by about 8%. The interpretation of whether this material contains branched chains is at best a statistical question since the confidence limits are not greatly exceeded. It will be shown later that values of M_w and η_0 for materials with low levels of LCB were located well above this power-law relationship. If Figure 6 is viewed on a scale as shown in Figure 5 to reveal the range of molecular weights over which the linear chain correlation was determined, these points would be indistinguishable from the confidence limit.

As was noted previously, there have been studies in the past that have shown that MWD had no effect on the power-law relationship for linear chains[25,30,33] and also studies which have shown an effect.[34,35] This study shows that MWD does not have an effect over the range studied ($2 \le M_w/M_n \le 10$); these results may be an improvement over many of the previous studies as a well-defined set of metallocene-based materials were examined, very precise measurements of η_0 and M_w were made, and η_0 was measured without the need of time-temperature superposition. There is no theory, to the best of our knowledge, which quantitatively predicts this insensitivity to the MWD. Nevertheless, this insensitivity can be applied to detect low LCB levels in polyethylene materials for a wide range of distribution breadths.

The MWDs for the 19 blends are shown in Figure 7. The six plots in this figure are scaled identically to enable straightforward comparisons. The plot in the upper left side is for a set of blend materials with contrasting levels (0–0.1) of LCB/1000C and similar distribution breadths ($M_w/M_n = 2$). All blend distributions are monomodal, symmetric about their peaks, and consistent with their design. Introduction of branched chains, at 0.005–0.1 LCB/1000C levels, is observed to have only a modest impact on their distributions. The distribution and its peak are found to shift to slightly lower molecular weights as the LCB/1000C value increases.

Similarly, results on the upper right side of Figure 7 are for a set of blends with contrasting levels (0–0.1) of LCB/1000C but with broader distribution breadths ($M_w/M_n = 4$). Again, all distributions are

consistent with the blend design, and these levels of LCB/1000C have only a modest impact on the distribution. However, in contrast to the distributions with $M_w/M_n = 2$, these distributions appear less monomodal and less symmetric, and the distributions also roughly superpose for the lower molecular weights ($M < 10^4$ g/mol). Three additional plots in Figure 7 contain results for other distribution breadths ($M_w/M_n = 6$, 8, and 10). In all cases, these LCB/1000C levels have only a modest impact on the distribution, the distributions are less monomodal and less symmetric, and the distributions roughly superpose at low molecular weights.

The plot on the lower right side of Figure 7 contains five distributions already displayed in the other plots. These distributions are for blend materials (B0P2, B0P4, B0P6, B0P8, and B0P10) prepared from the HDS set of materials. These materials also have similar M_w (126,000 ± 5,000 g/mol). Only one distribution (B0P2) is monomodal and symmetric. Elevating the distribution breadth from 2 to 10 is observed to shift the distribution and its peak to lower molecular weights.

A plot of the M_w and η_0 data is shown in Figure 8 for the blend materials. Results for all blend materials containing variations in MWD and LCB are well above the 95% confidence limit for linear-chain materials. Again, these results confirm the NMR results that these materials contain branched chains. The η_0 of the closest point (B1P2) to the 95% confidence line exceeds the line by 40%. The LCB/1000C level for this material is 0.005, and this value provides an indication of the detection limit for branched chains with η_0 and M_w data.

Quantification of the LCB level from the M_w and η_0 data remains challenging. One can see from the results in Figure 8 that the η_0 of any branched material progressively exceeds that of a linear-chain material with the same M_w as the LCB/1000C level is elevated at these low branching levels. However, the viscosity ratio η_0(branched chains)/η_0(linear chains) for any given M_w is expected to depend on the details of the diverse non-linear chain structures available to polyethylene materials. For example, one ideal class of non-linear chains restricts all branches to be attached to one main chain (backbone). The structure of these comb chains is summarized by three parameters: the backbone length, the branch length, and the functionality of the branch site. Identification of the impact of each parameter will require synthesis of numerous materials with well-defined structures and extensive studies of their M_w and η_0 data before and after blending with linear-chain materials. Another ideal class of nonlinear chains relevant to polyethylene allows branches to be attached to branches. These
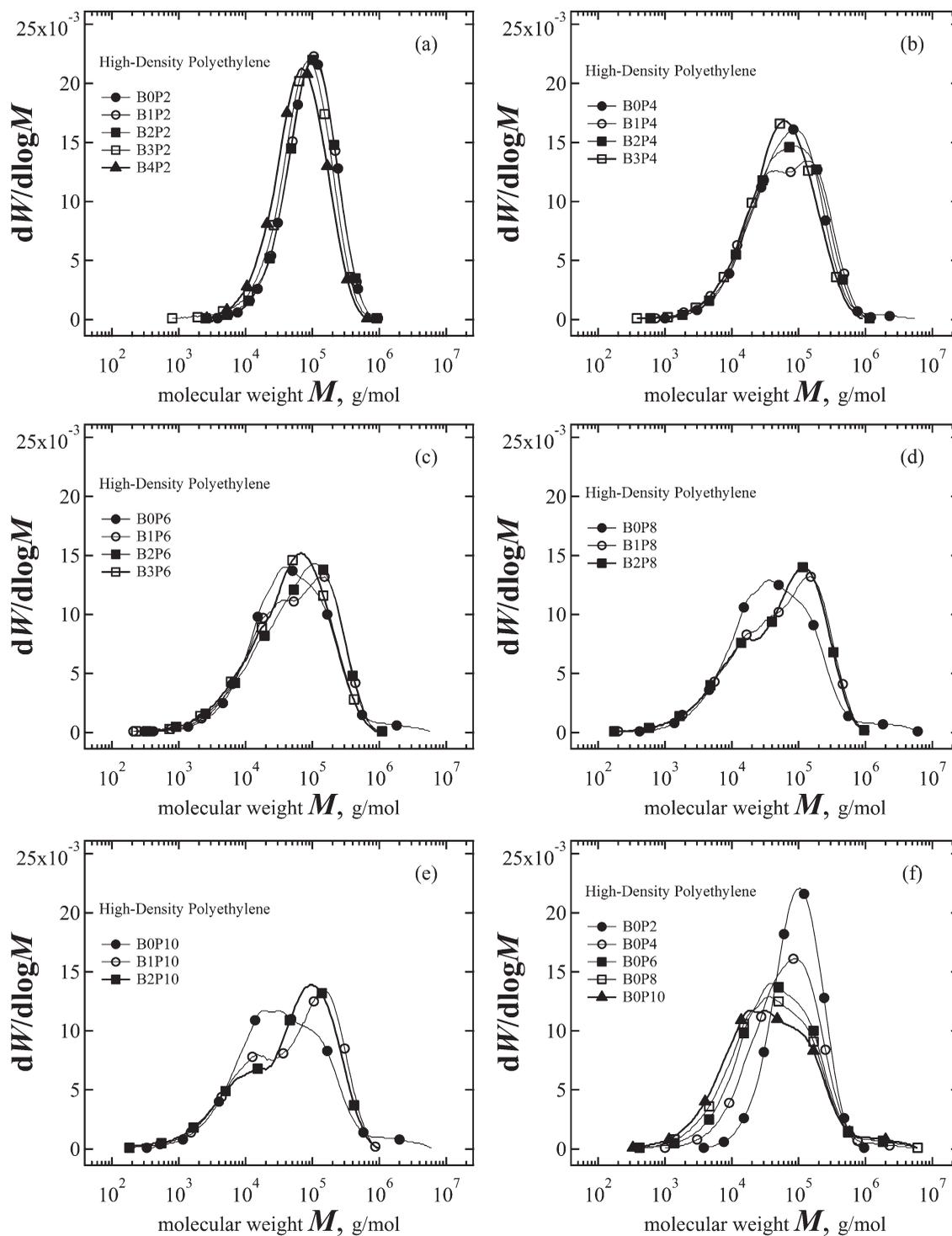
Figure 7 Molecular weight distributions of the high-density polyethylene blends.

tree chains are more complicated than combs and will require much more work to understand the impact of the chain structure on M_w and η_0 data. One may prefer also to study the viscosity ratio, η_0(branched chains)/η_0(linear chains), for any given absolute M_w, and for this reason the absolute M_w, measured by LALLS, is reported for most materials in Tables I and II.

CONCLUSIONS

An extensive set of metallocene-based high-density polyethylenes were prepared and blended to assess the impact of molecular-weight-distribution breadth ($2 \leq M_w/M_n \leq 10$) on the detection of low levels (0.005 LCB/1000C) of LCB. Values of M_w and η_0 for the linear-chain materials and their blends can be described
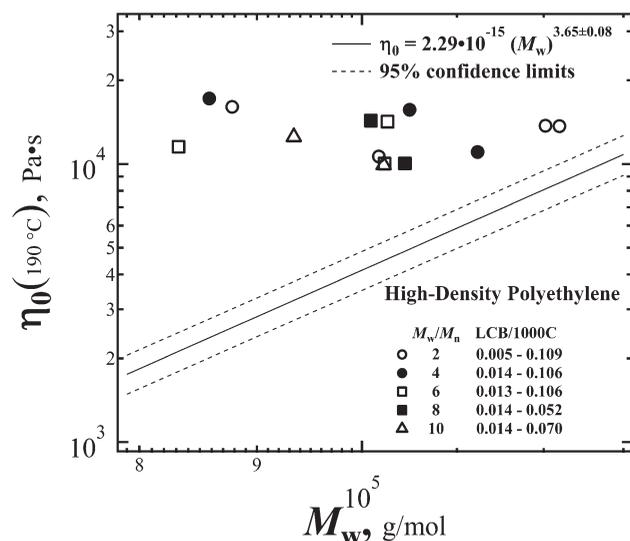
Figure 8 Dependency of the zero-shear viscosity, η_0, at 190°C on the weight-average molecular weight, M_w, for samples containing LCB and broadened molecular weight distributions; these samples are described more fully in Table II.

with a power-law relationship ($\eta_0[\text{Pa}\bullet\text{s}] = 2.29 \times 10^{-15} \times M_w[\text{g/mol}]^{3.65}$). In addition, values of M_w and η_0 for materials and their blends, prepared with low levels of LCB were located well above this power-law relationship. These differences were found to be enhanced when the zero-shear viscosities were determined using shear creep experiments with a constant-stress rheometer, and the molecular weights were determined using a conventional GPC method. Levels as low as 0.005 LCB/1000C can be detected regardless of the distribution breadth ($2 \leq M_w/M_n \leq 10$). This result simplifies the LCB analysis of many polyethylenes with M_w and η_0 data, since the distribution breadth need not be considered when $2 \leq M_w/M_n \leq 10$. This range of distribution breadth is sufficiently wide to include a substantial set of developmental and commercial materials. In conclusion, this approach, based on M_w and η_0, is a sensitive, robust, and rapid method to detect low levels of LCB in polyethylene materials and has been shown to be insensitive to whether the MWD breadth, M_w/M_n, rises from about two to ten.

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