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Assessment of NMR and Rheology for the Characterization of LCB in Essentially Linear Polyethylenes

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ABSTRACT: The identification and characterization of low levels of long-chain-branching (LCB) in essentially linear polyethylenes has attracted significant interest in recent years. One experimental technique is nuclear magnetic resonance (NMR), which can detect LCB in essentially linear polyethylene homopolymers for LCB in the range 0.2−3 branches per 10 000 carbon atoms. Another approach has been the use of a rheological measurement in combination with a dilute-solution measurement (intrinsic viscosity or GPC). NMR is a direct method of LCB measurement, but it provides no information on branch length and has other limitations related to interference from short chain branches. Rheology provides a sensitive but indirect method of measurement, capitalizing on the strong effect of LCB (longer than M_e, the entanglement molecular weight) on translational mobility of the polymer chains and thus viscosity. The purpose of the present work is to provide an assessment of the two approaches of LCB determination, using a series of well-characterized, essentially linear polyethylenes. NMR was shown to work satisfactorily in characterizing LCB for a series of metallocene-catalyzed polyethylenes, but it failed to detect LCB in other cases, including a series of linear polyethylenes where LCB was introduced deliberately via peroxide modification. A rheology-based index for LCB characterization was shown to be preferable, due to its robustness and general applicability in all cases examined.

Introduction

Conventional methods of determining long chain branching (LCB) from intrinsic viscosity (IV) in combination with gel permeation chromatography (GPC), or from NMR, seem attractive, because they yield results in terms of number of long-chain branches per given chain. However, in our earlier publication,[1] we showed that for low levels of LCB (~ 0.5−3/10 000 C), the ratio of the intrinsic viscosity of the branched polymer, $[\eta]_B$, to that of the linear polymer, $[\eta]_L$, of the same molecular weight is close to unity, within experimental error. The determination of LCB at these low levels then becomes prone to high error, since a small change in the ratio $[\eta]_B/[\eta]_L$ inherently means a large variation in LCB number. This is shown in Figure 1 (adapted from Figure 1 of ref 1), where the Zimm−Stockmayer prediction of LCB/10 000 C (eq 19 in ref 1) is plotted as a function of the intrinsic viscosity ratio, $[\eta]_B/[\eta]_L$, for two molecular weights (M = 50 000 and M = 150 000), in the range of essentially linear polymers, i.e., when the ratio $[\eta]_B/[\eta]_L$ is close to unity. A ratio $[\eta]_B/[\eta]_L$ greater than 0.95, for example, is indistinguishable experimentally from unity and yet the LCB/10 000 C level varies between 0.0 and 1.5 LCB/10 000 C (for $[\eta]_B/[\eta]_L$ between 0.95 and 1.0). Therefore, the Zimm−Stockmayer method of estimating LCB from the ratio $[\eta]_B/[\eta]_L$ cannot be employed reliably for essentially linear polymers ($[\eta]_B/[\eta]_L > \sim 0.9$).

The detection of LCB using on-line triple detectors[9] (light scattering, intrinsic viscosity, and refractive index) could give information about LCB as a function of molecular weight, i.e., by applying the Zimm−Stockmayer method on individual molecular weight fractions. While the sensitivity of the Zimm−Stockmayer method does improve at higher molecular weights (as the flattening of the LCB/10 000 C vs $[\eta]_B/[\eta]_L$ curve shows in Figure 1, at the higher molecular weight), the method will still encounter the quantitative uncertainties inherent in the Zimm−Stockmayer method, when applied to essentially linear polymers.

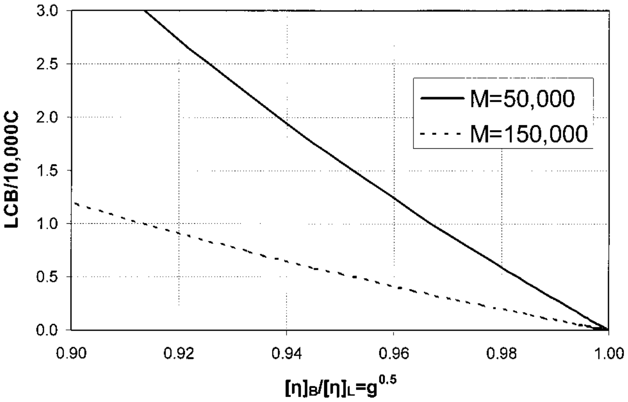

Figure 1. Dependence of the long chain branching, as determined by the Zimm−Stockmayer method, on the intrinsic viscosity ratio, at two different molecular weights and for essentially linear polyethlenes ($[\eta]_B/[\eta]_L > \sim 0.9$).

Nuclear magnetic resonance (NMR) spectroscopy provides another experimental technique for measuring LCB in polyethlyene. Even though NMR treats alkyl branches equal or longer than C_6 as long, several recent publications[2−4] from McMaster University have outlined an NMR method for obtaining low levels of long-chain branch density (LCBD), or the number of LCB/10 000 C, for ethylene homopolymers. Obviously, the NMR method cannot be used for copolymers of ethylene with octene-1, but we wish to point out here the limitations for several commercial high-density polyethylenes, which show low levels of long-chain branching.

Rheology provides another method, albeit indirect, for characterizing the presence of LCB in polyethylene, as shown in a series of recent publications,[5−8] including

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Table 1. HDPE Homopolymer Data

A. NMR and Rheological Data

							NMR data								
							C_4/10000C			R−CH═CH_2/10000C			≥C_6 (long)		
							Equistar			Equistar			Equistar		
sample	MI	E_R	[η] measd, dL/g	[η] GPC, dL/g	$\eta_o \times 10^{-5}$, P at 190 °C	LCBI from η_o and [η]	B250	V300	McMaster M300	B250	V300	McMaster M300	B250	V300	McMaster M300
M6210 (E0261)	1.0	1.9		1.64, 1.69	3.6	0.24	2.7		none	4.7		2.8	−0.59		0.74
6180 (I2PA53)	1.1	2.9	1.58	1.46, 1.49	3.9	0.32	1.1		none	9.8		10.0	2.2		3.0
6186 (I0KF53)	0.9	3.6		1.55, 1.50	8.2	0.56	1.9		3.6	8.2		5.8	2.4		0.53
6007 (I2FA51)	0.8	4.1		1.58, 1.50	13		0.38		none	6.9		8.0	0.86		1.2
748 (H2CS48)	0.7	4.8	1.57, 1.44	1.50, 1.51	30	1.0	0.56	2.3	1.4	6.5	7.3	5.3	1.1	0.21	0.59
							1.44			7.6			0.99		
6009 (332KA)	0.84	4.8	1.49,	1.31, 1.41	17	0.8	1.2	1.7		12.7	11.5		2.1	1.6	
6001 (I7SG51)	0.28	5.9	1.60	1.64, 1.61	114	1.4	1.2	2.0	0.84	7.2	7.0	6.4	0.60	0.27	0.58
							2.1			6.9			0.15		
							1.7			8.3			0.60		
6001C(I8UR53)	0.15	6.9	1.80	1.78, 1.80	624	1.9	none	1.1		8.0	6.8		1.2	0.89	
LS6040 (H3LC53)	5.5	0.46	1.22	1.20	0.20	0.005			none 2.5 ethyl			none			none
LS6040 + 250 ppm peroxide	4.5	0.80	1.22	1.19	0.25	0.05			none 2.5 ethyl			none			none
LS6050 + 500 ppm peroxide		1.5	1.24	1.14	0.60	0.20			none 1.8 ethyl			none			none

B. Molecular Weight and MWD data

sample	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-4}$)	M_z ($\times 10^{-4}$)	M_w/M_n	[η]$_{GPC}$
M6210	2.17 ± 1.3%	16.7 ± 3.0%	101 ± 2.8%	7.7 ± 1.8%	1.67 ± 2.1%
6180	1.15 ± 9.3%	14.0 ± 2.0%	95 ± 3.7%	12.3 ± 7.5%	1.48 ± 1.4%
6186	1.96 ± 5.1%	14.6 ± 3.9%	129 ± 0.6%	7.5 ± 0.9%	1.53 ± 2.3%
6007	1.97 ± 13.3%	14.6 ± 5.3%	97 ± 9.5%	7.5 ± 8.5%	1.54 ± 3.7%
748	1.82 ± 16.3%	14.4 ± 0.0%	105 ± 2.7%	8.1 ± 16.7%	1.51 ± 0.5%
6009	0.93 ± 14.5%	12.6 ± 7.3%	85 ± 0.8%	13.6 ± 7.3%	1.36 ± 5.2%
6001	2.03 ± 8.7%	15.8 ± 1.3%	102 ± 2.1%	8.8 ± 9.6%	1.63 ± 1.3%
6001C	2.33 ± 4.2%	18.0 ± 0.8%	107 ± 2.6%	7.8 ± 2.7%	1.79 ± 0.8%
LS6040	2.51 ± 1.1%	9.1 ± 5.5%	27 ± 8.0%	3.6 ± 3.9%	1.20 ± 3.5%
LS6040 + 250 ppm peroxide	2.43 ± 4.7%	8.9 ± 5.6%	25 ± 5.7%	3.7 ± 1.9%	1.19 ± 4.2%
LS6040 + 500 ppm peroxide	2.32 ± 5.5%	8.5 ± 1.7%	24 ± 3.0%	3.7 ± 5.8%	1.14 ± 0.0%

[a] NMR: B250 = Bruker 250 MHz, Equistar; V300 = Varian 300 MHz, Equistar; M300 = Bruker 300 MHz, McMaster University procedures and techniques developed by Wen-Jun Wang et al. of McMaster University (*Macromolecules* **1998**, *31*, 8677−8663). LCBI = $\{\eta_O^{0.179}/4.8 *[\eta]\} - 1.0$; [$\eta$] calculated from GPC used when measured data not available.

one by the present authors.[1] In particular, our previous publication[1] addresses a variety of rheological methods for determining LCB in polyethylenes.

The primary difficulty with the central theme of the present paper, namely the comparison of NMR LCB and rheological LCB, is that LCB has very different meaning for the two characterization methods. For NMR, LCB corresponds to chain lengths of six carbon atoms or greater, whereas for rheology, LCB corresponds to 270 (=M_c/14) carbon atoms or greater (M_c being the critical entanglement molecular weight for polyethylene). The ratio of 270/6 = 45 must mean than an agreement between the two methods, if found, must be fortuitous. This fact is apparently not self-evident to the characterization community, as indicated both by papers published in this journal[1−3,7,9] and in the patent literature.[11] It is the objective of the present work to show that rheology provides a consistently sensitive method of detecting LCB at a level around 0.2/10 000 C, whereas NMR has limitations in this range.

Experimental Section

Materials. The first group of eight resins, listed in Table 1A, are broad distribution, commercial high-density polyethylenes. All, except M6210, are made using Cr or modified Cr catalysts in Phillips slurry reactors. M6210 is a solution-polymerized resin using Ziegler−Natta catalysts using two or more reactors. The first six resins in this group are of similar melt index (MI) which is the melt flow rate (g/10 min) at 190 °C and using a load of 2160 g. The average molecular weights are thus also similar. The last two have lower MI. All of them were selected such that no comonomer was added during polymerization.

The second group of three materials are Ziegler-catalyzed, single reactor resins—the first of which, LS6040 (H3LC53), is made in the reactor and pelletized. The remaining two are derived from it by subjecting the pellets to an additional heat and shear history (extrusion) and adding 250 and 500 ppm of peroxide, respectively, thus deliberately introducing long-chain branching.

The molecular weight and molecular weight distribution data on all above resins are listed in Table 1B.

Characterization. ^{13}C NMR spectra on most of these resins were measured in the laboratory of McMaster University through the courtesy of Prof. A. Hamielec and Dr. W. J. Wang. The procedure for determining branching from these measurements has been extensively discussed in refs 2−5. McMaster used a slightly different procedure compared to the ones cited in this reference because many of the resins here surprisingly contained butyl side groups even though no comonomer was added during polymerization. The ^{13}C NMR measurements in our laboratory were made using the Bruker 250 MHz (proton frequency) and Varian 300 MHz (proton frequency) instruments and we adopted their method, except that we used a 4:1 ratio of TCB/D6B6 (1,2,4-trichlorobenzene and deuterated benzene) as the solvent and the sample concentration was 0.3 g/2.0 mL (compared to 0.6 g/2.0 mL in TCB, for the McMaster method).

Rheological measurements were made in the frequency range 0.025−398 rad/s and in many cases at various temperatures from 160 to 210 °C. The ARES rheometer made by

Rheometrics Scientific was used. The detailed procedure for such measurements is given earlier.[1]

Intrinsic viscosity, $[\eta]$, is derived from the measured relative viscosity at a concentration of 0.2 g/dl in TCB at 135 °C as discussed earlier.[1] It is also calculated from the molecular weight distribution data measured using the Waters model 150C gel permeation chromatograph (GPC). More details appear in an earlier publication.[1]

The rheological polydispersity index, E_R, is a measure of molecular weight distribution and/or long-chain branching but is essentially independent of molecular weight and the temperature of measurement. It is described in detail in ref 10 but discussed further in Appendix A. Limiting zero-shear viscosity is estimated using the Sabia equation fitted to the data of complex viscosity vs radian frequency as described earlier[1] and in Appendix B.

Results and Discussion

The rheological long-chain branching index, LCBI, is[1]

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

where η_o is the limiting, zero-shear viscosity at 190 °C and $[\eta]$ is the intrinsic viscosity in TCB at 135 °C. It is derived so as to be essentially independent of molecular weight (MW) and molecular weight distribution (MWD). It is very sensitive to even low levels of long-chain branching (LCB) because of the large influence of low level of long-chain branching in enhancing η_o.

Small or low levels of LCB have been known to be present in many commercial high-density polyethylenes (homopolymers and copolymers as given in refs 4−18 cited in ref 1). It is also present in the polyethylenes made by Dow's constrained geometry catalysts.[11] Inasmuch as rheological measurements are greatly influenced by MW, MWD, and LCB, it has been a challenge to separate the effect of MW and MWD from that of LCB, and nowhere has the challenge been greater than for those polyethylenes where LCB level is low such that the measured intrinsic viscosity is the same, within experimental error, as that calculated from the MWD data. We met that challenge by defining LCBI above, which is discussed in detail in ref 1. LCBI is superior to other rheological polydispersity indices such as E_R, discussed in ref 10, because the latter indices are influenced by both MWD and LCB, whereas LCBI is influenced by LCB alone. The further significance of LCBI is that it quantifies the enhancement in zero-shear viscosity due to LCB, by the factor of (1 + LCBI).[5,6]

For the purposes of the present work, we carefully selected several commercial, broad MWD high-density polyethylene samples, which had similar MW and MWD but showed a systematic increase in η_o and other rheological parameters such as E_R and had NMR measurements performed at McMaster University for the determination of long chain branching. Recent McMaster publications[2−5] indicate that for resins with $M_w \sim 100\,000$, $M_w/M_n \sim 2$, LCB levels as low as 0.2 branch/10 000 C or one long branch per 14 molecules, can be measured by NMR even though we realize that NMR considers chains equal to or greater than C_6 in length as "long".

To our surprise, we find that many of these polymers (in the first group of eight, in Table 1A) contain small levels of short-chain, butyl branches, even though no hexene-1 as a comonomer was added during polymerization. Such a level of C_4 branches means that the 34.5 ppm resonance in the NMR signal contains contributions from both the butyl branch and the "long" branch ($\geq C_6$). Specifically, the 34.5 ppm resonance is from two $\alpha\delta^+$ butyl plus three $\alpha\delta^+$ C_6 or longer branches. The butyl branch resonance (from C_4 carbons) occurs at 34.1 ppm, as a shoulder on the 33.9 ppm stronger resonance due to end vinyl group—as shown in Figure 2. Therefore, McMaster University researchers proposed LCB from NMR for sample 6001 to be calculated as follows:

$$\mathrm{LCB}(\geq C_6)/10\,000 = \left\{\frac{451 - 2 \times 111}{3} \times 10\,000\right\}/\mathrm{IA}_{\mathrm{total}} \tag{2}$$

where $\mathrm{IA}_{\mathrm{total}}$ is the total intensity of all carbons, 451 is the intensity of the 34.5 ppm resonance (due to $C_4 + C_6$ or longer branches), and 111 is the intensity of the 34.14 ppm resonance (due to C4 branches). Figure 2a is a highly magnified NMR spectrum in the narrow range 33.5−39.5 ppm, obtained while keeping the baseline flat and as noise-free as possible. One can see from Figure 2a that there is uncertainty in such a determination, because of the subtraction of two similar intensity resonances and from the further uncertainty in the intensity value for C_4 resonance since it does not occur at exactly the same location in the spectra from our laboratory as shown in Figure 2b.

The relevant part of the typical spectrum from our laboratory is shown in Figure 2b (using Bruker 250 MHz) and Figure 2c (using Varian 300 MHz). The spectrum in Figure 2b is not as clean in Figure 2a, and Figure 2c is even noisier than Figure 2b. Also there is more baseline drift in the spectrum of Figure 2c. Therefore, it is not surprising that the agreement in values for C_4 and long branches in Table 1A from the two laboratories is not good.

It is further evident from the data in Table 1A that LCB level from NMR, either from ours or McMaster laboratory, does not relate at all to the systematic increase in η_o or rheological polydispersity measure E_R or to the rheological long-chain branching index derived from η_o and intrinsic viscosity or the distribution of relaxation times as shown in Figure 3.

Among the NMR LCB data from McMaster, 6180 shows the highest level of LCB (3/10 000 C). However, all the available rheological data (η_o , E_R, LCBI etc.) indicate that the level of LCB is low compared to other resins in the group. Further evidence that NMR LCB level is suspect comes from the data on isothermal crystallization rate as discussed in another publication.[12]

To test the measurement reproducibility, six unlabeled samples of 6180 were given to McMaster University for multiple LCB measurements by NMR. The data in Table 2 show that the precision is good—95% confidence limits of 23% at an average level of 3.3/10 000 C.

We avoided the uncertainty caused in NMR LCB determination by butyl branches and chose a narrower distribution (M_w/M_n ~4.5), Ziegler−Natta catalyzed, high-density homopolymer resin. The base resin, which is pelletized, contains essentially no LCB (either by rheology or by NMR). However, even when we deliberately introduce LCB by peroxide treatment with 250 and 500 ppm peroxide, no LCB is detected. Large increases in η_o (Figure 4), E_R, and distribution of relaxation times (Figure 5) are observed, as expected.

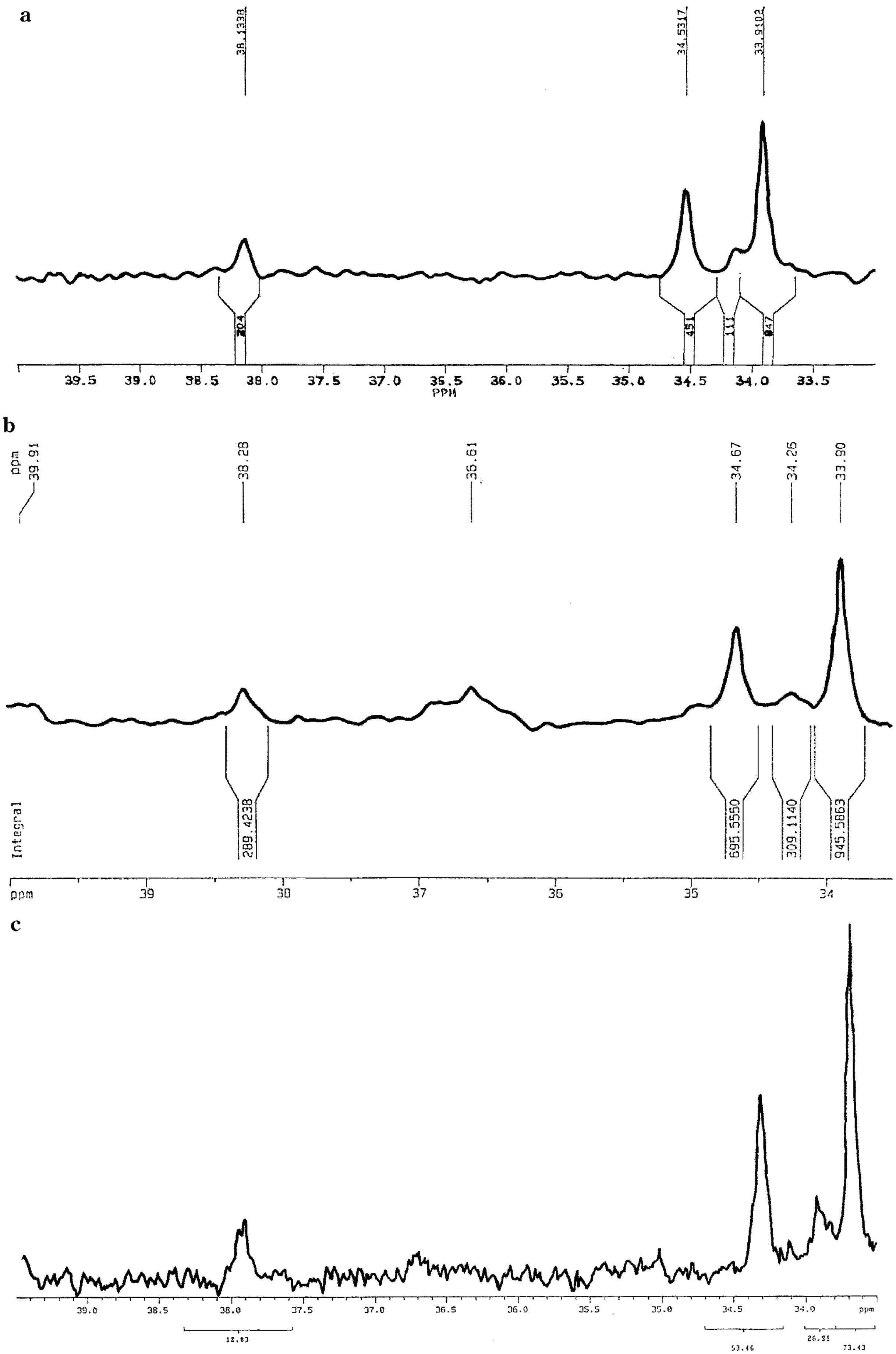

Figure 2. NMR spectrum on sample 6001 determined with three different instruments: (a) Bruker AC 300, at McMaster University; (b) Bruker 250 MHz at Equistar; (c) Varian 300 MHz at Equistar.

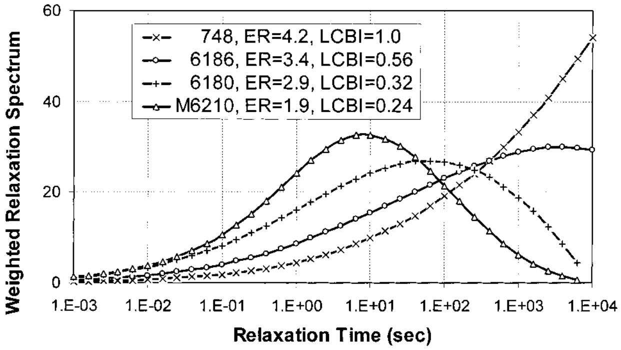

Figure 3. Weighted viscoelastic relaxation spectrum ($\tau H(\tau)/\eta_0$) for four resins from Table 1, with increasing rheological polydispersity and long chain branching index.

Table 2. Repeatability Studies on HDPE Homopolymer for Long-chain Branching (L) and Terminal Vinyl (V): Results from McMaster University, Sample 6180 (I2PA53), 1.1 MI, 0.960ρ

L/10000 C	V/10000 C
3.5	9.3
3.5	10.1
3.4	9.0
3.5	8.5
2.8	8.5
3.0	10.0
av: 3.3	9.2
std dev: 0.31	0.70
95% confidence limits: 23%	19%

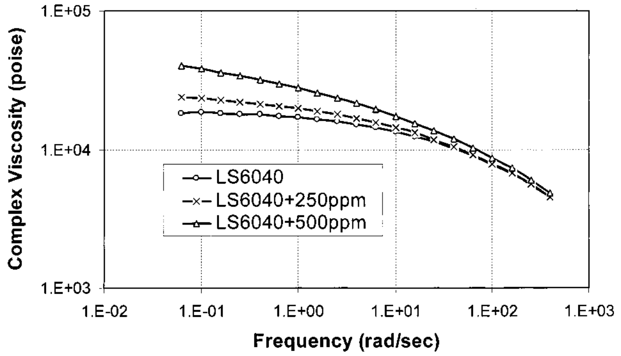

Figure 4. Effect of peroxide addition (250 and 500 ppm) on the dynamic viscosity of LS6040.

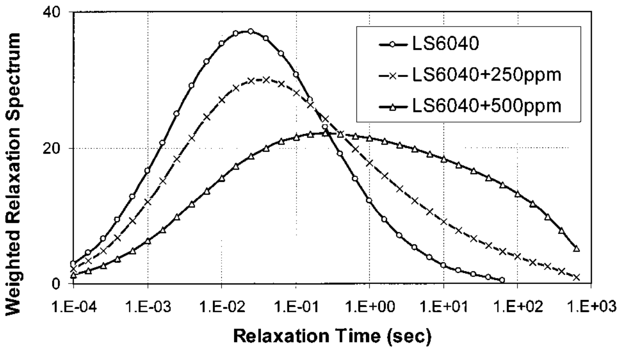

Figure 5. Effect of peroxide addition (250 and 500 ppm in LS6040) on the weighted viscoelastic relaxation spectrum (τ H(τ)/η_0).

Table 3. Melt Viscosity and Long-Chain-Branching (by NMR), Data of Ref 5

LCB/10000 C	η,[a] P	M_w
0.0	1.7×10^5	120 000
0.20	2.1×10^5	125 000
0.22	2.6×10^5	100 000
0.35	7.9×10^5	108 000
0.40	12.3×10^5	107 000
0.44	17.0×10^5	110 000

[a] At 0.01 s^{-1}, 190 °C.

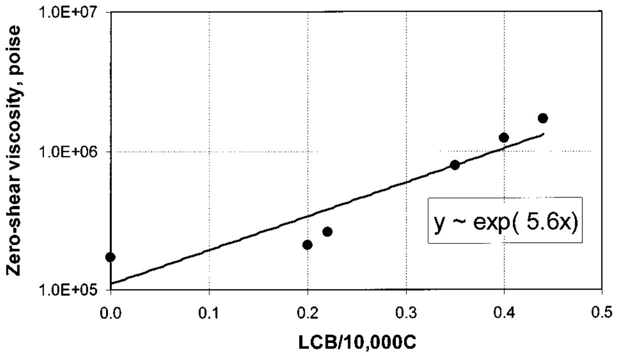

Figure 6. Effect of LCB on zero-shear viscosity showing a dramatic sensitivity of viscosity on LCB (data from ref 5).

A similar lack of sensitivity to changes induced by thermal and shear history was seen in the NMR data obtained previously in our laboratory. Here the Cr-catalyzed polymer, 6009, had undergone multiple-pass extrusion. No difference in LCB levels by NMR was seen from the base resin to the one which was re-extruded three times. However, η_o increased from 1.3×10^6 to 2.3×10^8 P, LCBI increased from 0.76 to 3.55, E_R increased from 4.2 to 5.7, and MI decreased from 0.84 to 0.60. As expected, these large changes in rheological properties accompanied such great changes in both the weight and diameter swell during blow molding of bottles that it was impossible to make 90 g 1 gallon dairy bottles with complete handles for the multiple-pass extruded samples.

Even more evidence exists in the literature, which shows a much greater sensitivity of rheological measurements to small changes in low levels of long-chain branching. For example, let us consider the data[5] from McMaster University on metallocene-catalyzed polyethylenes, made using Dow's constrained geometry catalyst, given in Table 3. The zero-shear viscosities are plotted against LCB (determined by NMR) in Figure 6. One can see a dramatic (exponential power) dependence of η_o on the number of long-chain branches. Therefore, even in a select group of metallocene-catalyzed polyethylenes, where a correlation between the rheological property and the NMR-determined number of long-chain branch is seen, the tremendous advantage and sensitivity of the rheological property is evident.

Effect of Length of LCB. It is difficult to leave the subject of measurement of long-chain branching by NMR without citing the issue raised by Wang et al.[4] For example, Dow's patent[11] reports a value of NMR LCB of 3.4/10 000 C for a metallocene-catalyzed resin without comonomer, $M_w/M_n = 2.1$, I_2 or MI = 1.18 and $I_{10}/I_2 = 11.8$. No value for η_o is reported. However, Wang et al.[3] note that a resin with similar M_w/M_n and I_{10}/I_2, they obtain only 0.22 number of long-chain branches per 10 000 carbon atoms, i.e., 1 order of magnitude lower level of LCB, despite the fact that I_2 is nearly half the I_2 in the Dow patent (LCB generally increases with decreasing I_2). Therefore, there may be a factor of 10 discrepancy in the number of long-chain branches in one of the labs (Dow's or McMaster's), or as Wang et al. speculate, there is a difference in the length of the long-chain branch, with a longer branch causing a greater increase in I_{10}/I_2 and η_o. If the latter indeed is the case, then it is even more problematic for chemists to obtain the NMR number of long-chain branches and relate them to the rheological properties such as I_{10}/I_2, η_o, and the distribution of relaxation times, all of which govern their processability and the physical properties of the fabricated parts. It is difficult to resolve this factor of 10 difference because Dow's commercial polyethylenes are ethylene copolymers with octene-1 as a comonomer, and since C_6 branches are counted as long, one cannot measure long chain branching by NMR on such samples.

Conclusions

For broad distribution, commercial high-density polyethylenes, NMR at its best provides qualitative information about long-chain branching. The quantification by NMR for such polymers is problematic and unsatisfactory. Six resins in this study were carefully selected to have similar molecular weights and molecular weight distributions but showed a large and systematic increase in zero-shear melt viscosity and consequently in the rheological long-chain branching index (LCBI) developed earlier. However, the number of long chain branches determined by NMR showed random scatter. Additionally, NMR could not detect any LCB in peroxide-modified HDPE or any change in multiple pass extruded HDPE, whereas large changes in rheological behavior were seen. Even the analysis of literature data on metallocene-catalyzed polymers reveals that rheology is the preferred method of LCB characterization, due to the dramatic sensitivity of zero-shear viscosity on the number of long-chain branches.

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Appendix A: Rheological Polydispersity Measure E_R

The definition and justification of this measure of rheological polydispersity was given in ref 10, but a brief description is included here for completeness. E_R utilizes linear viscoelastic data of storage modulus, G', and loss modulus, G'', in the frequency range of 0.0158−400 rad/s. E_R is independent of MW and temperature of measurement, but it is influenced by MWD and LCB.

E_R is extracted from G' vs G'' data at the two lowest decades of frequency.

$$E_R = [C_1 G'] \quad \text{at } G''_{\text{ref}} \tag{A1}$$

where G''_{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''_{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.

Appendix B: Zero-Shear Viscosity Estimation Using the Sabia equation

The limiting low-shear or zero-shear viscosity η_o is estimated using the Sabia equation fit of dynamic complex viscosity η^* vs radian frequency ω

$$\log(\eta^*/\eta_o) = (\eta^*/\eta_o - A)\log[1 + (\omega/\omega_o)^B] \tag{B1}$$

with the parameters $\eta_{o,}$ ω_o, A, and B, where ω_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 proposed and Shida and Cote later implemented a computer program to let the A value float because of the wide range of MWD encountered.[10] The value of product $AB = 0.72$, which is related to the limiting slope of η^* vs ω $(-AB)$, is kept fixed, based on the fundamental consideration from Graessley's theory, which predicts a steady flow viscosity having a constant limiting slope with respect to shear rate and from the consideration that complex viscosity vs ω is analogous to steady flow viscosity vs shear rate behavior. Sabia, Nakajima, and Shida and Cancio 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.[10]

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