Complementarity of Universal Calibration SEC and ^{13}C NMR in Determining the Branching State of Polyethylene

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ABSTRACT: The quantitation of long-chain branching (LCB) and short-chain branching (SCB) in polyethylene (PE) was accomplished with a combination of carbon nuclear magnetic resonance (^{13}C NMR) spectroscopy and size exclusion chromatography (SEC) with universal calibration. We demonstrate how the spectroscopic and chromatographic techniques can supplement each other, as neither is capable individually of completely describing the molecular architecture imparted by the various types of branching. The essential lack of impact of SCB on the hydrodynamic volume imposes a limit on SEC for determining this type of branching, whereas highly effective LCB in the PE molecule may not offer a statistically large enough amount of long chains for accurate determination by NMR. A variety of examples are given for PE, showcasing the advantages and shortcomings of each analytical method and their complementarity. Additionally, the importance of choosing an appropriate linear standard and viscosity shielding ratio (ϵ) for the Zimm–Stockmayer branching calculations employed for analyzing SEC data is emphasized with an examination of the effect on the results of using a branched standard and various ϵ values. © 2000 John Wiley & Sons, Inc. J Polym Sci B: Polym Phys 38: 3120–3135, 2000

Keywords: long-chain branching; short-chain branching; size exclusion chromatography; universal calibration; carbon nuclear magnetic resonance (^{13}C NMR); polyethylene; linear standard; viscosity shielding ratio

INTRODUCTION

Polymer branching in general and of polyethylene (PE) in particular has been an area of intense research for several decades. As branching is intrinsically related to the chemical and physical properties of a molecule, the presence of short-chain branching (SCB) affects the crystallinity, chemical reactivity, hardness, glass-transition temperature, and so forth, whereas long-chain branching (LCB) has a more pronounced effect on viscoelastic properties such as the intrinsic viscosity, sedimentation behavior, and angular distribution of scattered radiation of dilute solutions, as well as the viscosity and elasticity of melts.

A variety of analytical techniques have been used over the years to study the different types of branching present in synthetic and natural polymers, including spectroscopic,[1–7] chromatographic,[6–10] flow,[11,12] computational,[10,13] and enzymatic[14,15] methods. The last of these, though highly useful, is generally limited to the realm of natural polymers. Regarding the first three methodologies, carbon nuclear magnetic resonance (^{13}C NMR) spectroscopy is highly sensitive to SCB and mid-chain branching but typically cannot distinguish branches of 6 carbon atoms or more from one another (this range was recently extended to 10 carbons with field strengths of 750 MHz).[3] Size exclusion chromatography (SEC) and

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rheological measurements are both sensitive to LCB in the molecule at branch lengths of about 20 carbon atoms or more. It thus becomes evident that no single analytical technique can uniquely describe the complete branching state of a macromolecule.

For PE, in which long-chain and short-chain branches may both be present, depending on the polymerization process, the choice of the catalyst utilized in production, or both, a combination of several of the aforementioned techniques is a promising means of obtaining a clearer morphological picture of the polymer. The combination of ^{13}C NMR and multidetector SEC for the PE branching problem, as discussed in the literature of the late 80s and early 90s,[6,7] led researchers to the conclusion that spectroscopically obtained data should serve as the benchmark to which all other branching data should be compared. More recently, however, Guan et al.[16] showed that these techniques measure different molecular properties and also demonstrated dangerous shortcomings of the spectroscopic characterization route. In studies of Pd/α-diimine-catalyzed PE, structures with negligible changes at the short-chain level ranged from linear to hyperbranched with respect to their dilute solution behavior governed by LCB interactions.

In this article, we present examples of various PEs in which the use of both ^{13}C NMR and SEC is critical to accurately describing the branching state of the molecules, as the use of either technique alone would lead to incomplete or, in some cases, incorrect conclusions.[6,7,16] SEC with universal calibration, in which an online viscometer is incorporated into the experimental setup, was used to assess LCB. The importance of choosing an appropriate linear standard for the LCB calculations is also demonstrated by the use of both known linear and known branched materials as the references, whereas the need to adequately understand the draining characteristics of the polymer in solution are evidenced in the dependence of the ratio of the mean-square radii on the viscosity shielding ratio.

EXPERIMENTAL

Materials

All polymers were purchased commercially and analyzed without further purification. These included NBS 1475 and NBS 1476 PEs [U.S. Department of Commerce, National Bureau of Standards (now National Institute of Standards and Technology), Washington, DC], PE 52 and PE 88 PEs (Polymer Standards Corp., Mentor, OH), and PE 081 PE (Polysciences, Warrington, PA) with narrow polydispersity polystyrene standards (Polymer Laboratories, Amherst, MA). Solvent materials included 1,2,4-trichlorobenzene (TCB; Burdick & Jackson, Muskegon, MI), *o*-dichlorobenzene-d_4 (Isotec Inc., Miamisburg, OH), and Santonox (Aldrich, Milwaukee, WI).

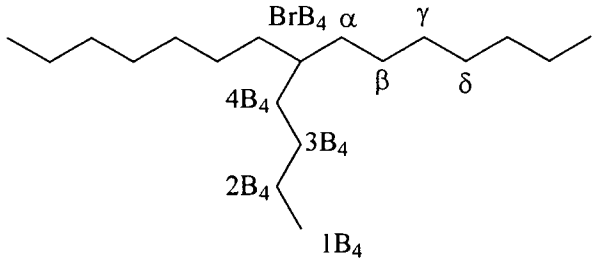
^{13}C NMR

^{13}C NMR spectra were collected with a Varian Unity Inova 500 NMR spectrometer with a 5-mm ^{1}H–^{19}F/^{31}P–^{15}N switchable solution probe at 150 °C. The solutions were prepared for analysis by the dissolution of approximately 75 mg of each sample in 650 μL of *o*-dichlorobenzene-d_4. The samples were dissolved by being heated in an oven at 130 °C for 6 h. NMR spectra were collected spinning at 20 Hz with 1200 repetitions, a 90° pulse width, a 20-s recycle delay with WALTZ-16 decoupling (a composite pulse decoupling scheme consisting of 16 90° RF pulses) only during acquisition (to suppress any NOE enhancement), and a spectral width of 32,500 Hz (260 ppm). NOE (Nuclear Overhauser Effect) enhancement provides non-uniform enhancement of the various ^{13}C NMR peaks, and needs to be suppressed for quantitative NMR work. Processing was done with no-zero filling and an exponential line broadening function of 2.5 Hz. All spectra were referenced by the setting of the main-chain PE peak to 30.000 ppm.

A recycle delay of 20 s is not long enough to obtain fully quantitative results, according to the work of Hansen et al.[1] However, it is long enough to obtain semiquantitative results and is sufficiently long that for most carbons the results are indeed fully quantitative. NOE enhancement was avoided because NOE enhancements could be significantly different for the various carbon species present.

The ^{13}C NMR assignments used in this work are listed in Table I. They were taken from the work of Hansen et al.[1] and Kaji et al.[2] We chose to use the numbering system of Hansen et al., in which the branch itself is numbered, starting from the methyl group and counting back to the main chain, and includes the length of the branch; the branch methine carbon is numbered for the length of the branch; and the main chain is

lettered relative to the distance from the branch. An example is shown next for a four-carbon branch:



A more rigorous lettering system for the main chain is to refer to the distance from the branch carbons in both directions (i.e., $\alpha\delta$ would be adjacent to one branch and four carbons from a branch in the opposite direction on the polymer chain), but there was no evidence in this work that the branches were sufficiently close to make such an additional complication necessary.

With the previously cited articles, the amount of *n*-butyl (B_4) branches was calculated via the $4B_4$ peak at 34.29 ppm and the $2B_4$ peak at 23.37 ppm. The amount of *n*-hexyl and longer branches (B_6+) was calculated via the BrC_6+ peak at 38.32 ppm, the αB_6+ peak at 34.71 ppm, and the βB_6+ and $5B_6$ peaks at 27.39 ppm after correction for the B_4 contribution (five carbons). The amount of chain ends was calculated via the $1B_6+$ peak at 14.03 ppm, the $2B_6+$ peak at 22.85 ppm, and the $3B_6+$ peak at 32.18 ppm after correction for the contribution from the B_6+ branches (three carbons). All peak areas were normalized to the total integrated carbon count and multiplied by 1000. No ethyl (B_2) branches were observed for any of the PEs in this study, although they were observed for other PEs not listed here with the same experimental setup.

SEC

Samples were analyzed on a high-temperature SEC system (Model 150C, Waters, Milford, MA) equipped with a differential refractive index detector and retrofitted with a differential viscometry detector (Model 150R, Viscotek, Houston, TX). The detectors were connected in parallel. The temperatures in the injector and column compartments were maintained at 135 °C. The temperature in the pump/solvent compartment was maintained at 50 °C. Data acquisition and manipulation were performed with a Viscotek DM 400 data manager and Viscotek TriSEC GPC software (version 3.0, revision B.01.01).

Samples were dissolved in TCB with 1.5 mg/mL Santonox (3-*tert*-butyl-4-hydroxy-5-methyl-phenyl sulfide) added as an antioxidant. The sample concentration was 1–2 mg/mL, the injection volume was 300 μL, and the run time was 55 min. Separation occurred over a column bank consisting of three analytical columns (PLgel mixed C, Polymer Labs) preceded by a guard column (PLgel 10-μm precolumn, Polymer Labs). The mobile phase was TCB/Santonox at a flow rate of 1.0 mL/min. The solvent/mobile phase was filtered before sample preparation through a 0.2-μm nylon filter (Phenomenex, Torrance, CA). TCB/Santonox (10 mL) was added to 10–20 mg of the samples; this solution was heated at 135–150 °C for several hours with stirring, until solutions appeared clear to the eye. No filtration of the samples was performed.

Universal calibration, whereby the logarithm of the hydrodynamic volume (i.e., intrinsic viscosity × molecular weight) was plotted against the retention time (or volume), was performed with a series of narrow polydispersity polystyrene standards ranging in their peak-average molecular weights from 1700 to 2,300,000 Da. Two injections per standard were performed. A linear plot ($r^2 = 0.9998$) was obtained with a third-order fit. Fluctuations in the flow rate were corrected with the solvent/air peak present in all samples in comparison to the same peak in a duplicate solvent blank. Universal calibration allowed for the absolute molecular weight averages and distributions to be determined by the generation of a calibration curve based on the hydrodynamic volume of the standards that was independent of

Table I. ^{13}C NMR Peak Assignments for PEs

Structure	Chemical Shift (ppm)
BrB_4, BrB_6+	38.32
αB_4, αB_6+	34.71
$4B_4$	34.29
$3B_6+$	32.18[a]
γB_4, γB_6+	30.51
Main chain CH_2, $3B_4$, $4B_6$ (right shoulder)	30.00
$5B_6$, βB_4, βB_6	27.39
$2B_4$	23.36
$2B_6+$	22.83[a]
$1B_4$, $1B_6+$	14.03[a]

[a] Includes chain ends.

chemical or morphological differences between the unknown and the calibrants.[17]

RESULTS AND DISCUSSION

The ^{13}C NMR spectra of the five PE samples studied are shown in Figures 1–5. Figure 6 shows the molecular weight distribution overlay of all the samples, and the amount of SCB in each compound is given in Table II. Molecular weight and dilute solution data, determined by SEC with universal calibration, are given in Tables III and IV. The importance of the requirements for choosing an appropriate linear standard is addressed at the end of this section.

NBS 1475

This is a well-known broad molecular weight distribution linear PE standard. Its linearity was confirmed in our laboratory with both methods of analysis (see Fig. 1 and Tables II and IV). Neither SCB nor chain ends were observed spectroscopically (Table II), and the Mark–Houwink curve of the intrinsic viscosity versus the molecular weight shows no deviations from linearity (Fig. 7). Consequently, this served as the linear standard for all the LCB calculations. The molecular weight averages obtained by our methodology (Table III) proved quite similar to those obtained previously by independent groups.[6,18,19]

LCB results were derived from SEC data according to the theory developed by Zimm and Stockmayer.[20] Branching ratios (g), weight-average branching numbers (B_n), and weight-average branching frequencies (λ), given in Table IV, were derived via TriSEC software with the following relations (the subscript w, referring to weight-average quantities, was omitted for the sake of simplicity, and all branching data herein should be considered weight averages):

$$g = 6/Bn\{0.5[(2 + Bn)/Bn]^{0.5} \times \ln\{[(2 + Bn)^{0.5} + Bn^{0.5}]/[(2 + Bn)^{0.5} - Bn^{0.5}]\} - 1\} \quad (1)$$

$$\lambda = RBn/M \quad (2)$$

$$g' = g^{\varepsilon} \quad (3)$$

$$g' = ([\eta]_B/[\eta]_L)_M \quad (4)$$

$$g = \{([\eta]_B/[\eta]_L)_M\}^{1/\varepsilon} \quad (5)$$

The equations for trifunctional ($f = 3$) branching were used, as the NMR data gave no indication of tetrafunctional branching being present in any of the samples. The R term in eq 2 corresponds to an arbitrary repeat-unit value. Here, we chose $R = 14{,}000$ to make λ read as branches per 1000 carbons. (M in eq 2 corresponds to the molecular weight of the chromatographic slice under consideration, which was assumed to be monodisperse). The subscripts B and L in eqs 4 and 5 correspond to the branched polymers (or polymers of unknown branching status) and linear polymers, respectively, whereas the subscript M in these same equations refers to the fact that the intrinsic viscosities ($[\eta]$) are being compared at the same molecular weight. The branching ratio g is known in the literature as the ratio of the mean-square radii of the unknown polymer and the linear standard, and it is most conveniently determined with multi-angle (or, less conveniently, variable-angle) light scattering photometry. This ratio is related to the ratio of the respective intrinsic viscosities by the Debye/Bueche viscosity shielding ratio, ϵ. The latter depends not only on the identity of the polymer under consideration but also on the solvent and temperature, and it is indicative of the draining characteristics of the polymer in solution.[21,22] The literature value for ϵ of 0.75 was used in our calculations because it was determined for PE under identical experimental conditions (1,2,4-TCB, 140 °C);[18,23] this is discussed later in *On the Choice of a Linear Standard*.

NBS 1476

Figure 2 is the NMR spectrum of NBS 1476, a broad molecular weight distribution branched standard. This sample had a high degree of SCB, the branches consisting of a mix of butyl, hexyl, and longer branches. There were no ethyl branches present, and the chain ends were significant in quantity (Table II). The absence of any ethyl branches was somewhat surprising, given the work of Pang and Rudin.[6] Regarding LCB, the branching number and branching frequency of this sample were both an order of magnitude greater than for NBS 1475 (Table IV). The dissimilar dilute solution behavior of the two NBS samples may be observed in Figure 7. Although the branching number (B_n) increased with the

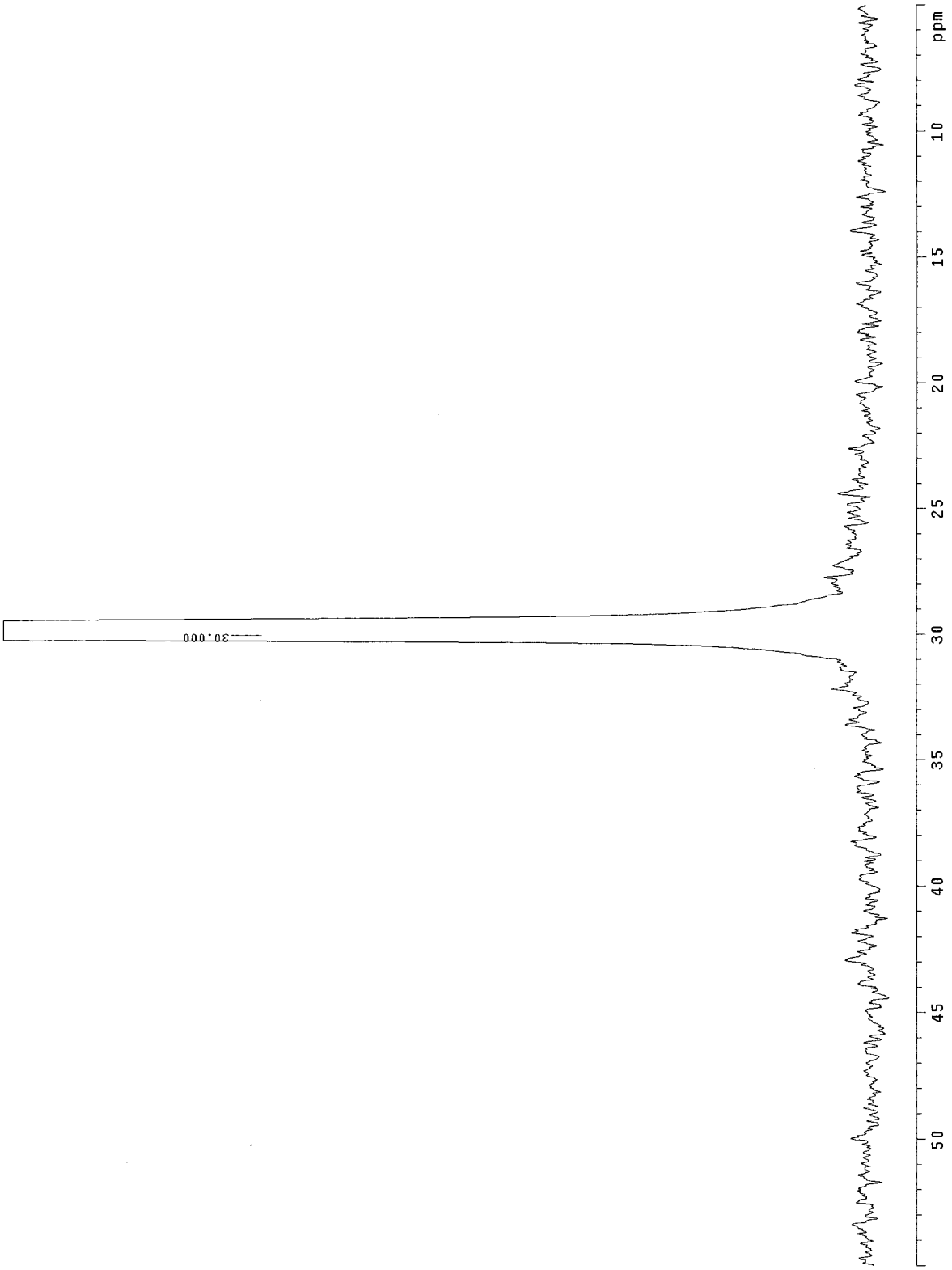


Figure 1. ^{13}C NMR spectrum of NBS 1475.

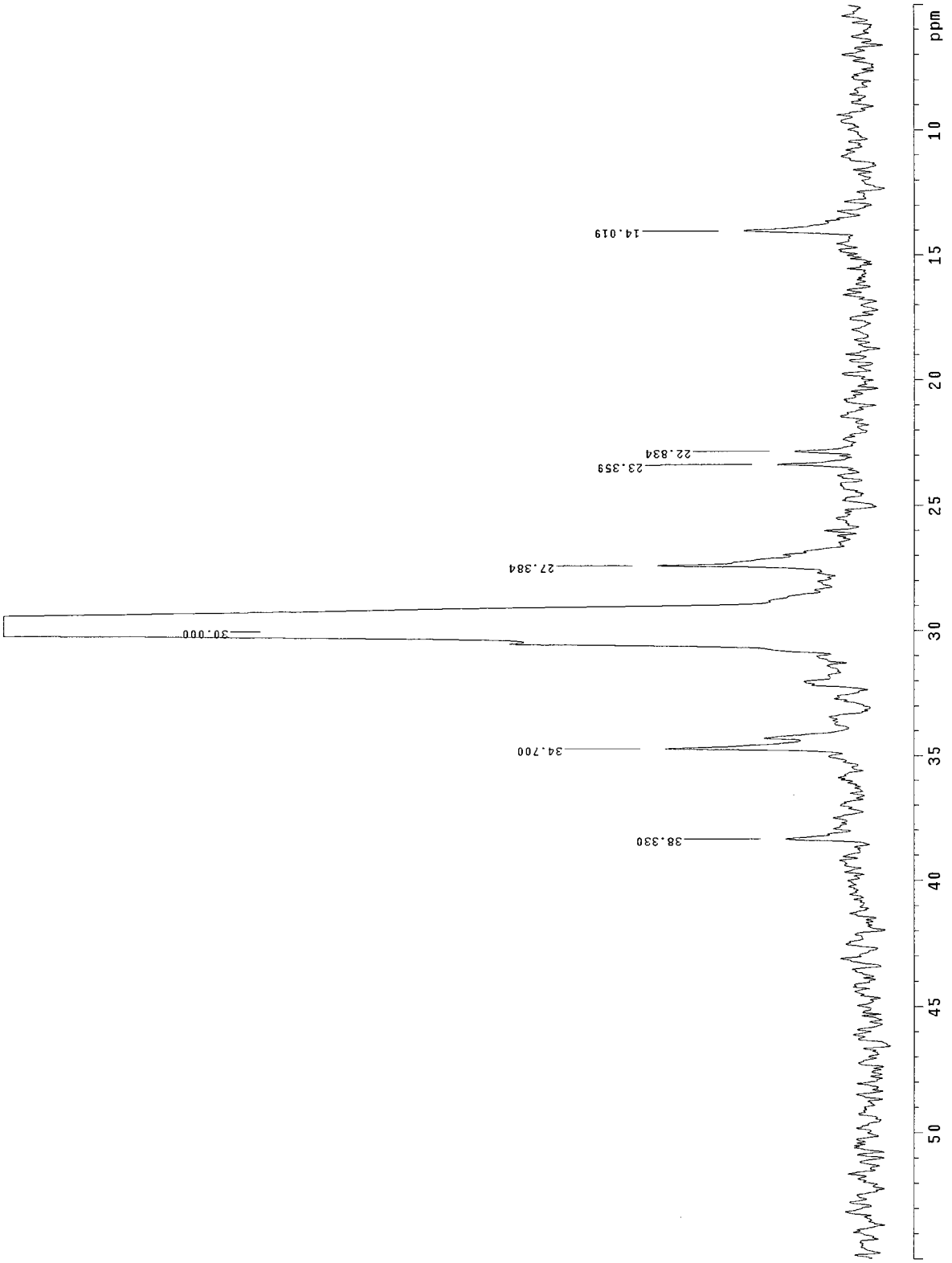


Figure 2. ^{13}C NMR spectrum of NBS 1476.

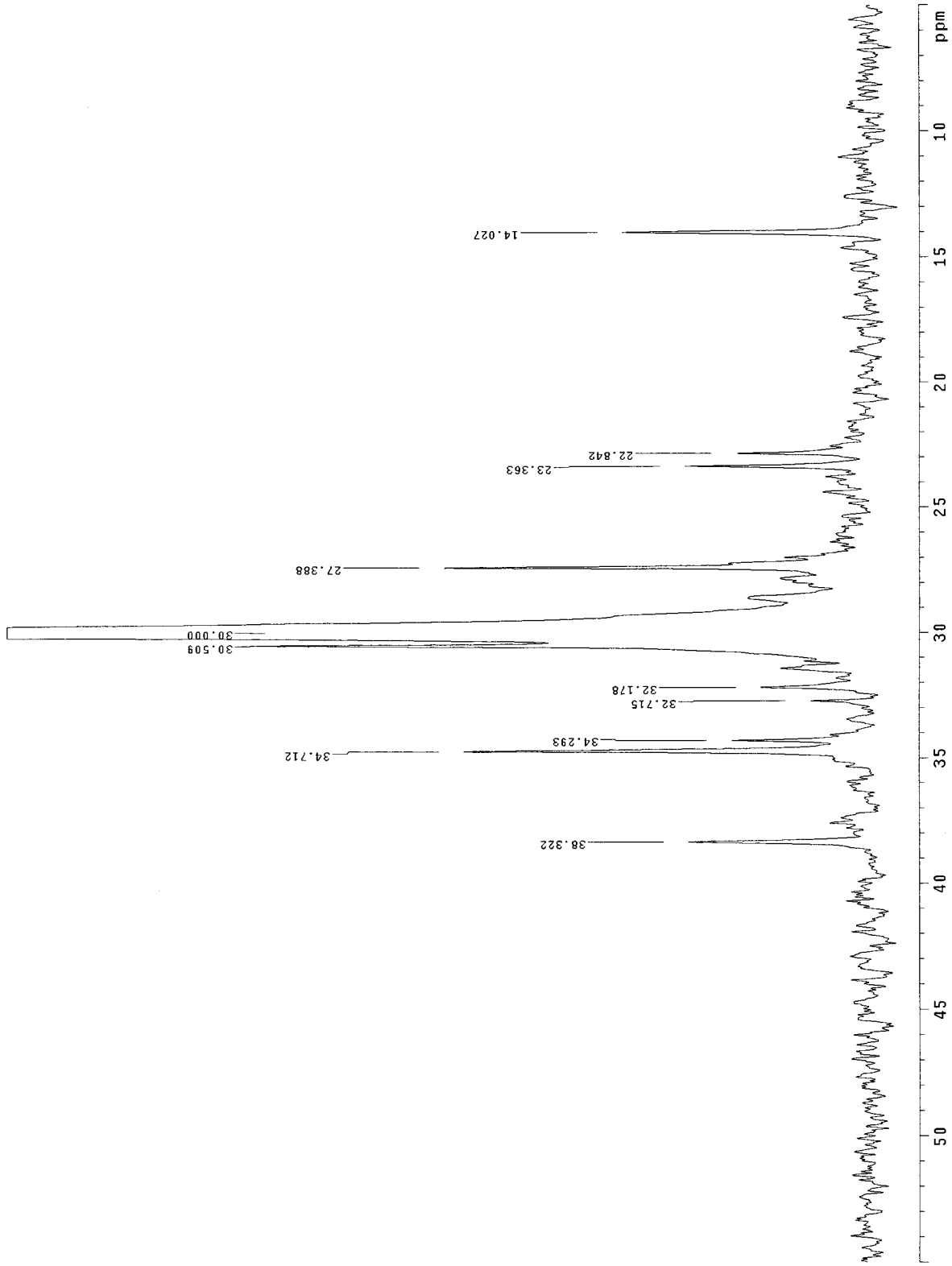


Figure 3. ^{13}C NMR spectrum of PE 081

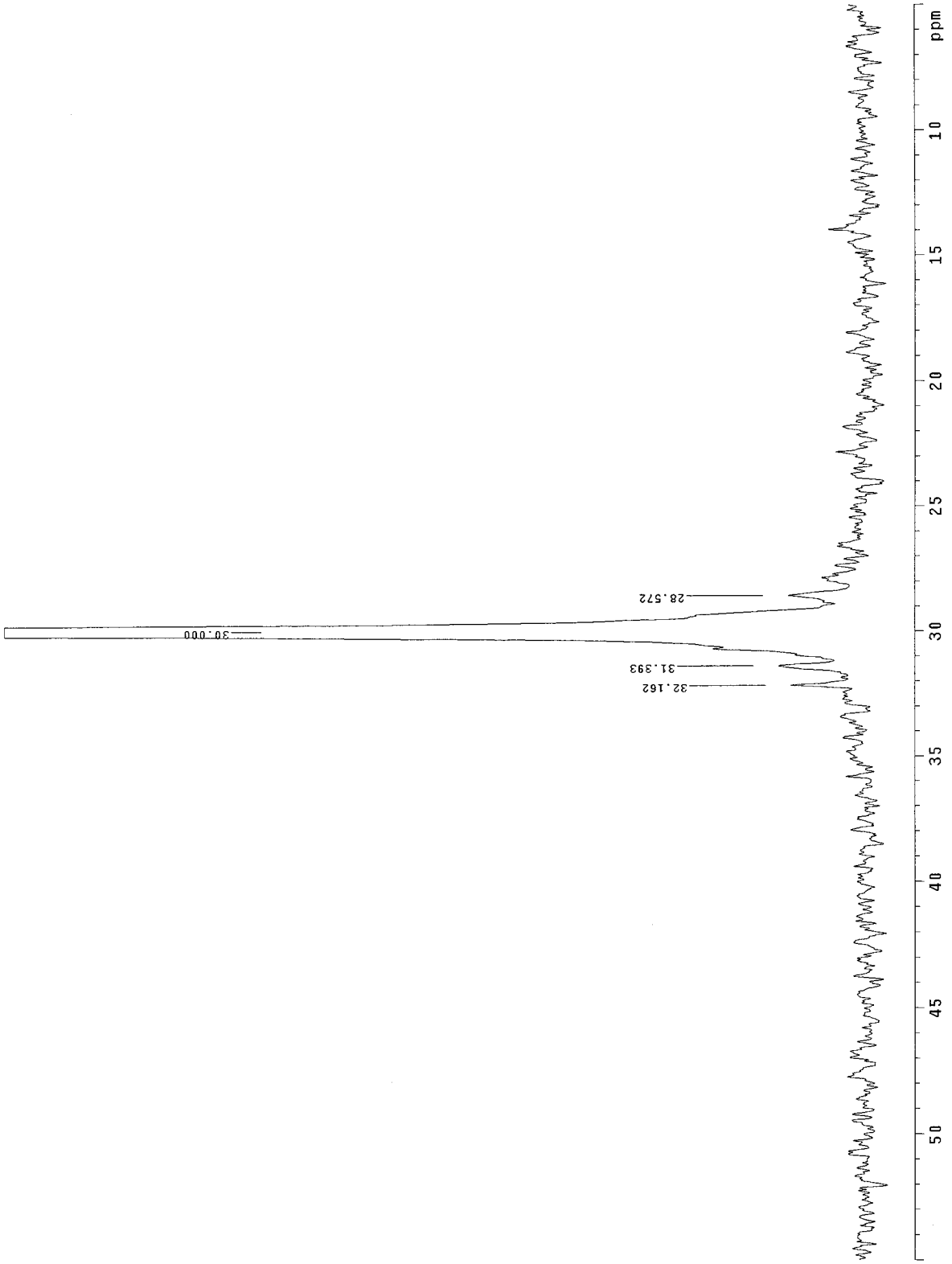


Figure 4. ^{13}C NMR spectrum of PE 52.

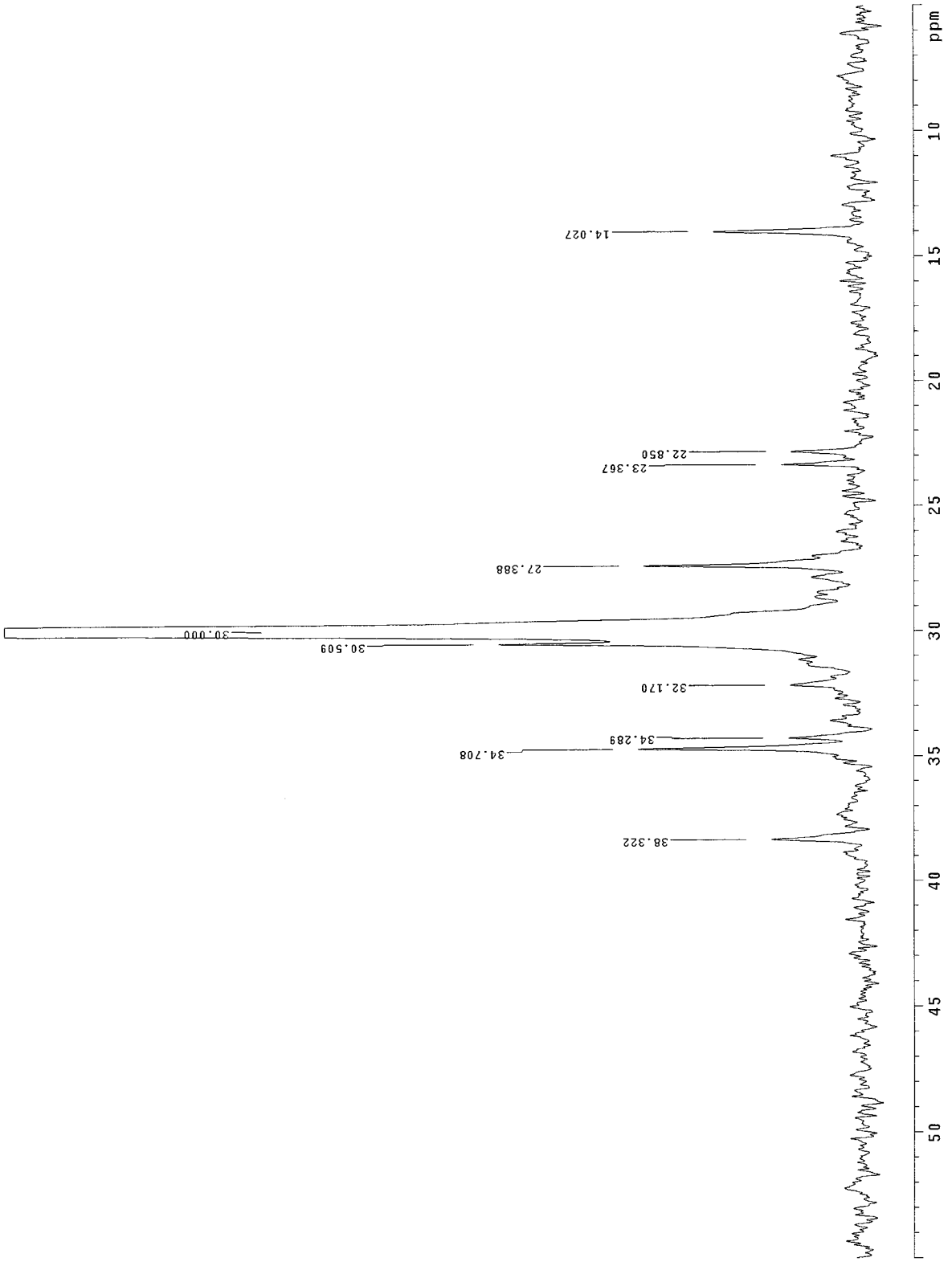


Figure 5. ^{13}C NMR spectrum of PE 88.

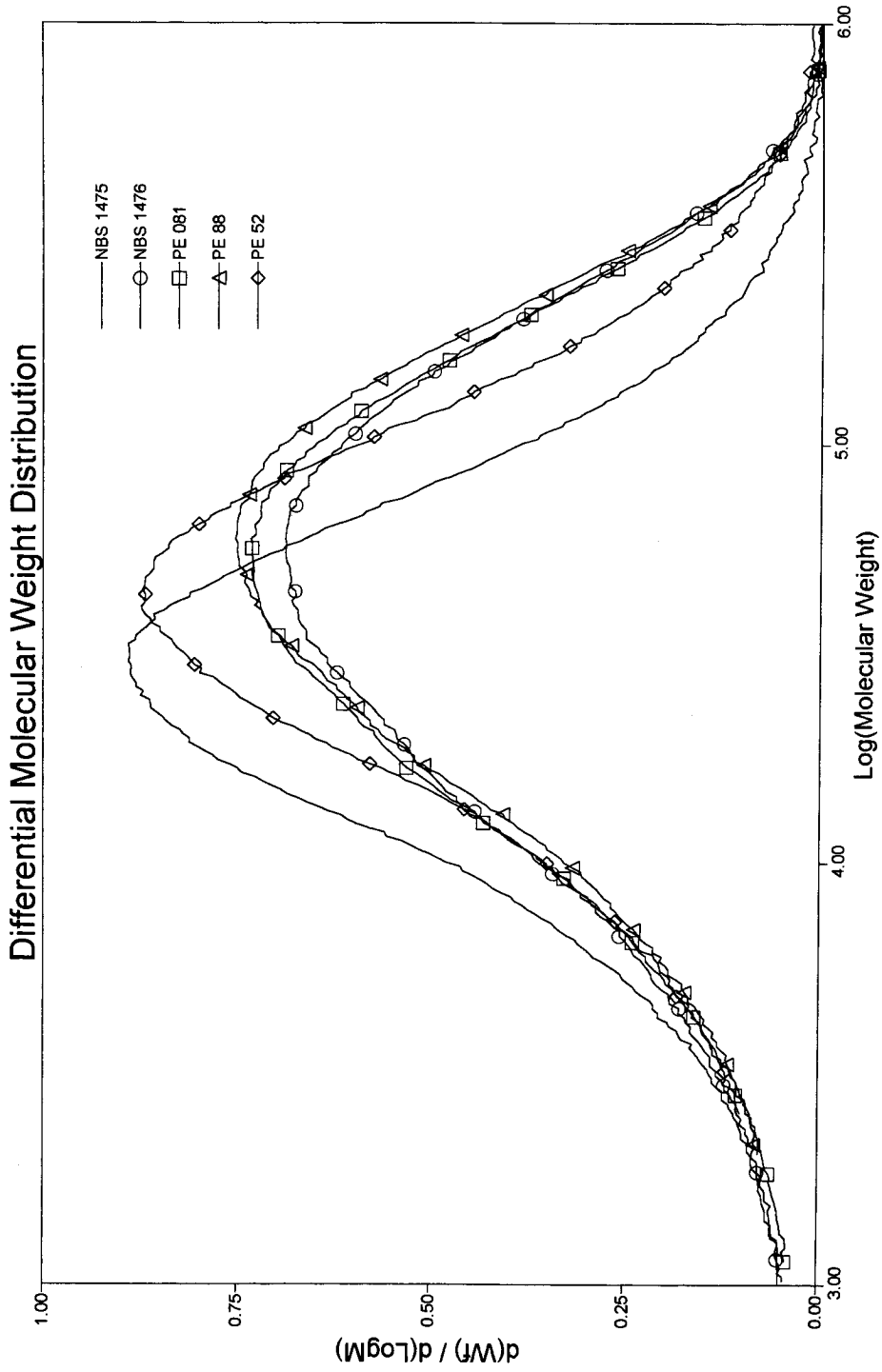


Figure 6. Molecular weight distribution overlay of the PE samples.

Table II. ^{13}C NMR-Measured SCB[a]

Sample	Butyl	Hexyl+	Chain Ends
NBS 1475	0.00	0.00	0.00
NBS 1476	6.96	3.40	3.34
PE 88	4.79	6.29	0.48
PE 081	7.95	2.70	2.33
PE 52	0.00	0.00	0.00

[a] No other branch types (e.g., methyl, ethyl, and amyl) were observed by ^{13}C NMR. See text for details.

increasing molecular weight of NBS 1476, thereby accounting for the downward curvature in the plots of $[\eta]$ versus the molecular weight and g versus the molecular weight, the branching frequency (λ) of this sample remained constant. The molecular weight averages obtained for this sample (Table III) were lower than the literature values, although these latter values should be taken with skepticism because they vary from 76 KDa to more than 220 KDa for the weight-average molecular weight, hardly a consensus.[24] Additionally, the high-molecular weight shoulder observed for this sample with the use of online light scattering detection[6,24] was not evidenced by either the differential refractive index or the differential viscometry traces (note the absence of this shoulder in the molecular weight distribution of NBS 1476 in Fig. 6).

PE 081

The NMR spectrum of PE 081 is shown in Figure 3. This sample had a substantial amount of SCB and LCB (Tables II and IV). On the basis of the molecular weight and dilute solution data given in Table III, as well as the molecular weight distributions of both samples, PE 081 and NBS 1476 appeared to be identical. The branching data, both long-chain and short-chain, allowed differences to be established. The LCB data in Table IV indicate PE 081 was more highly branched than NBS 1476 at this level, although on the basis of the amount of chain ends in Table II, we would expect the opposite trend. The differences in both cases, however, were relatively small, and a more striking example follows.

PE 52

On the basis of the NMR spectrum of this sample (Fig. 4), it should have been fairly linear because it contained essentially no butyl or hexyl branches (Table II) or any measurable amount of chain ends. SEC analysis indicated that this was a highly branched sample at the long-chain level (Table IV). The drawback of using NMR to measure LCB stems from the fact that if the branching is highly efficient (i.e., the percentage of branches that form long-chain branches is very high), then the total amount of branch carbons to which ^{13}C NMR is sensitive is quite low, making branching difficult, if not impossible, to detect.

It was useful for the purpose of end-use properties to examine the differences in the SCB and LCB of PE 52 and PE 081. Both of these samples were shown by SEC to possess a high degree of LCB. NMR analysis, however, demonstrated much SCB in PE 081 and none at all in PE 52. Therefore, when deciding which one of these two PEs to employ, one should take into account the expected performance characteristics of the products.

PE 88

^{13}C NMR analysis of this sample (Fig. 5 and Table II) indicated a fairly large amount of butyl branches and a high amount of hexyl branches in comparison with the other PEs in this study. That the amount of chain ends was measurable and the hexyl branch content was high indicates that this polymer had both fairly short chains and fairly

Table III. Molecular Weight and Dilute Solution Data for PEs

Sample	M_w (Da)	M_n (Da)	M_w/M_n	$[\eta]_w$ (dL/g)	Rg_w (nm)	a
NBS 1475	51,100	12,700	4.02	0.75	9.8	0.6
NBS 1476	72,800	16,800	4.42	0.81	11.8	0.5
PE 88	86,400	24,200	3.57	0.81	12.3	0.5
PE 081	74,600	17,700	4.21	0.80	11.6	0.5
PE 52	66,200	21,300	3.11	0.78	11.1	0.6

Table IV. Branching Data for PEs

	Linear Standard (NBS 1475)[a]			Branched Standard (NBS 1476)[b]		
Sample	g	B_n	λ	g	B_n	λ
NBS 1475	0.985	0.147	0.033	—	—	—
NBS 1476	0.812	1.642	0.381	0.992	0.046	0.018
PE 88	0.674	3.321	0.724	0.884	0.864	0.275
PE 081	0.771	2.006	0.312	0.990	0.056	0.006
PE 52	0.763	1.788	0.596	0.928	0.482	0.246

[a] The data were generated with eqs 1–5 and NBS 1475 as the linear standard. See text for details.
[b] The data were generated with eqs 1–5 and NBS 1476 as the linear standard. See text for details.

efficient LCB. The NMR value of the chain ends was corrected for branch ends and thus reflects only the two end groups on the base molecule and not the end groups on the branches. SEC analysis showed that PE 88 possessed the largest amount of LCB, having a lower g value and higher B_n and λ values than any other sample (Table IV). The large amount of LCB in PE 88 indicates that for this sample the hexyl branches, as measured by ^{13}C NMR, correlated well with the SEC measurements of LCB because of efficient LCB.

On the Choice of a Linear Standard

As mentioned earlier, the branching equations used for LCB calculations stem from the classic 1949 publication by Zimm and Stockmayer.[20] Some limitations and restrictions of these calculations were recognized by the authors at the time, who also outlined the requirements of an appropriate linear standard. Because the determination of LCB by SEC is the topic of a recent review,[22] only a cursory overview is given here before the experimental results.

For a comparison of mean-square radii (i.e., when calculations are based directly on g), a linear standard should

1. Be devoid of any appreciable amount of long-chain branches. Interestingly, although no SCB would also be ideal in this situation, SCB was shown to have a minimal effect on space-filling macromolecular properties (e.g., intrinsic viscosity).
2. Have the same chemistry as the material under consideration to eliminate differences in bond lengths, torsional angles, molecular expansion/contraction in solution, and so forth.
3. Cover the molecular weight region of interest so that comparisons may be performed at equal slices of M (the subscript in eqs 4 and 5). As can be seen in Figure 6, NBS 1475 fulfills this requirement. Alternatively, a comparison of the molecular weights at equal elution volumes may be performed.[22,25]
4. The functionality (f) of the branch points (e.g., trifunctional, $f = 3$, or tetrafunctional, $f = 4$) should be known a priori so that the appropriate branching equations may be chosen (only the equations for $f = 3$ are given in this article). Although f should remain uniform throughout the molecule, the calculations were shown to be invariant to changes in the length of the branches over the breadth of the molecular weight distribution.

An added imposition on these calculations, when viscometric detection methods are used such as here, is the need to have an appropriate value for ϵ, the Debye/Bueche viscosity shielding ratio. ϵ is related to the draining behavior of the polymer in solution and is dependent on the chemistry of the polymer being considered as well as the solvent used and the temperature of the experiment, as these all affect coil contraction and expansion.[21,22] ϵ falls in the range 0.5–1.5, with the smaller value determined by Zimm and Kilb[26] to correspond to non-free-draining, high molecular weight, regular stars and the larger value determined by Berry[27] for comb-shaped polystyrenes in good solvents. The majority of values for this constant fall in the range 0.7–0.8.[22,23] A value for the shielding ratio may be derived from the slope of a plot of g versus g', if the benefits of both multi-angle light scattering

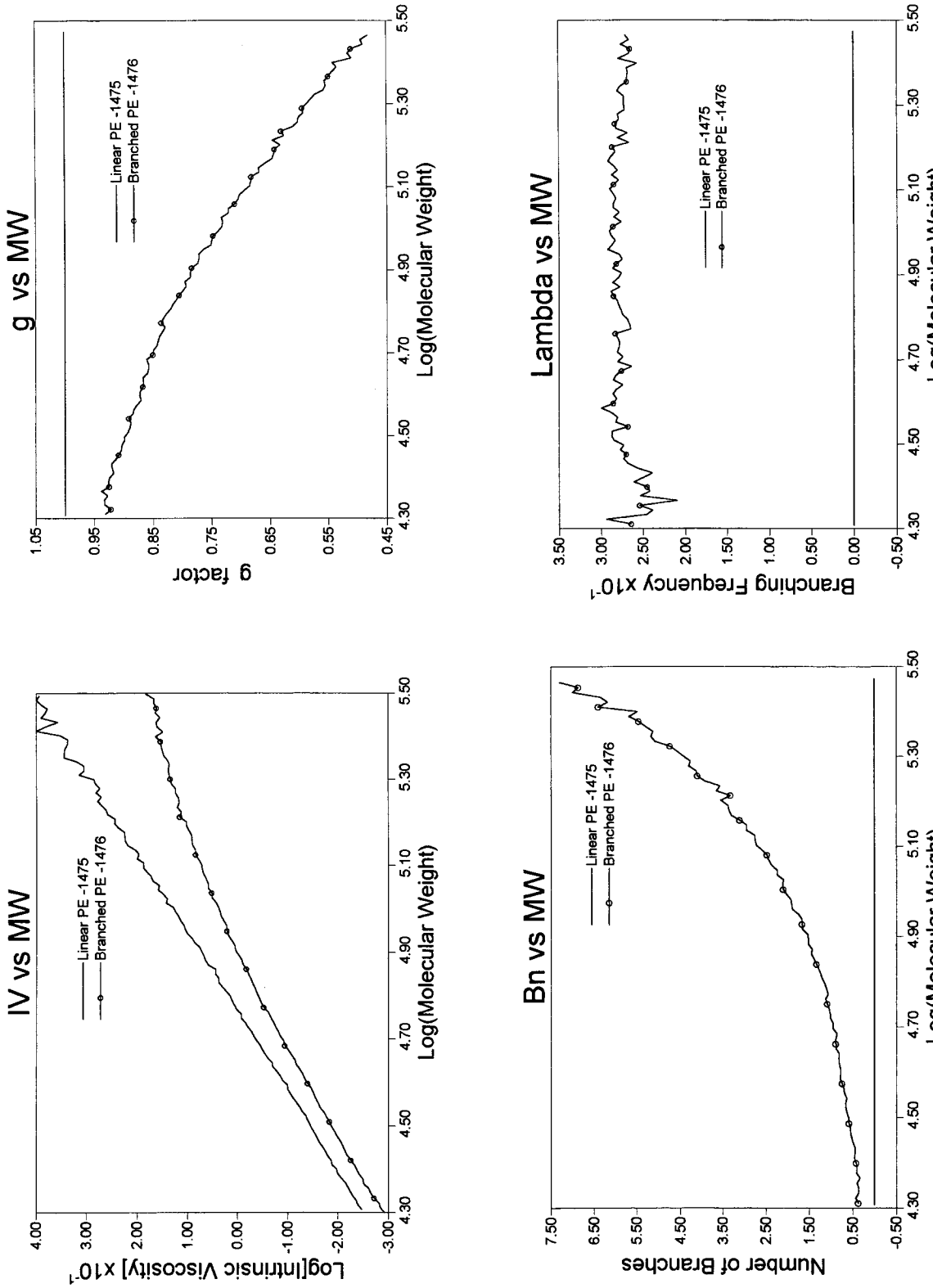


Figure 7. Branching characteristics of linear NBS 1475 versus branched NBS 1476. Clockwise from the top left are Mark–Houwink plots of the intrinsic viscosity (IV) versus the molecular weight (MW), the branching ratio (g) versus MW, the branching frequency (λ) versus MW, and the branching number (B_n) versus MW. The abscissa is scaled in all the plots to show the regions of greatest difference between the samples.

Table V. Effect of ε on g

Sample	g ($\varepsilon = 0.75$)	g ($\varepsilon = 0.5$)	g ($\varepsilon = 1.5$)
NBS 1475	0.985	0.978	0.993
NBS 1476	0.812	0.731	0.901
PE 88	0.674	0.554	0.821
PE 081	0.771	0.677	0.878
PE 52	0.763	0.666	0.873

and viscometry are available, although multi-angle light scattering would likely obviate the use of g' in the branching calculations. Recently, the dependence of ϵ on the molar mass has also been introduced as an additional nontrivial variable not taken into account here.[19,28] The ratio of the intrinsic viscosities (eqs 4 and 5) was used instead of the ratio of the Rg values listed in Table III. The reason for this is that the latter are not true (i.e., measured) root-mean-square radii, as would be obtained from scattering experiments, but were instead derived from viscometric data according to the Flory–Fox/Ptitsyn–Eizner methods outlined in the literature.[29–31]

The importance of carefully choosing an appropriate linear standard is addressed here through a comparison of the LCB results based on the well-characterized NBS 1475 linear PE and data generated when merely one of the requirements was ignored. As mentioned previously, we used a value for ϵ of 0.75 that was determined previously for PE by other researchers under identical experimental conditions.[18,23] An incorrect understanding of the draining of the polymeric coil leads to choosing a wrong value for ϵ, the result of which is shown in Table V. We chose the extremes of the range of ϵ to highlight the effect of this constant on the ratio of the mean-square radii (g), on which the calculations of B_n and λ are based. As can be seen in Table V, the effects were small for the linear PE NBS 1475 and became more pronounced with increasing branching. Moreover, to the best of our knowledge, no values for ϵ have been published for dendritic macromolecules of any kind, these being polymers with the largest amount of branching theoretically achievable. Because of the optimization of branching in this type of structure[10,32,33] and the effect of branching, branch density, and possible solvophobic interactions of the terminal groups of dendrimers on the minimization of coil draining in dilute solutions, we expect the ϵ value for dendrimers to be lower than the Zimm/Kilb value for non-free-draining stars.

The data on the right-hand side of Table IV were generated with NBS 1476, the broad molecular weight distribution branched PE sample used as the linear standard. This was done to demonstrate the consequences of erroneously or indiscriminately picking a compound as a standard for the purpose of LCB calculations. As can be observed in a comparison of the right and left sides of Table IV, if the chosen material happened to consist of even a moderate amount of long chains, the results for all the samples under consideration were greatly affected. In the worst case, the branching frequency of PE 081 was reduced by almost two orders of magnitude when NBS 1476 was used as the standard, making this sample appear, on the basis of all the indicators (g, B_n, and λ), linear. The need to be assured of the linearity of the standard used is obviously of paramount importance when LCB is quantitated by chromatographic methods.

We chose to use the equations for $f = 3$ on the basis of the absence of any tetrafunctional branching in the NMR spectra of all the PEs studied. As noted previously, however, if a small amount of very long tetrafunctional branches were present, the spectroscopic method employed would not be likely to detect these. If one couples the absence of $f = 4$ signals in all of the spectra with what is known about PE synthesis,[34–38] however, the possibility of tetrafunctional branching is greatly reduced. The effects on LCB calculations arising from a misunderstanding of branching functionality have been demonstrated elsewhere in the literature.[7]

CONCLUSIONS

The complementarity of the chromatographic and spectroscopic approaches to quantitating polymer branching was demonstrated here with various PE samples. Linear to highly branched PEs at both the short-chain and long-chain levels were characterized by ^{13}C NMR and SEC with universal calibration. Samples with substantial LCB had no appreciable SCB, and the lack of chain ends or branch carbons determined by NMR was not necessarily an indication of an absence of long-chain branches in the polymer.

Also illustrated here was the importance of exercising extreme care in choosing a linear standard for the purposes of LCB calculations. If a

sample that is believed to be linear but is actually not is chosen as a standard, the effect on the results can be disastrous, even if the chosen sample possesses only a moderate amount of LCB. Likewise, an awareness of the draining characteristics of the particular polymer under consideration and under a given set of experimental conditions was shown to be important for the purposes of determining LCB by SEC with universal calibration. An incomplete understanding of the permeability of the polymer molecule to the streamlines of the solvent flow leads to choosing an incorrect value for ϵ, the viscosity shielding ratio, on which all viscometrically derived LCB calculations are dependent.

A gray area of branching remains to be examined, that area pertaining to branches with lengths between 10 and 20 carbon atoms. This range is below the sensitivity of any of the commonly employed SEC detectors, and no improvement is foreseen from this side of the branching barrier either chromatographically or rheologically. From the other side of this artificial barrier, the continuous increases in the NMR fields being used have already allowed for branch lengths of up to 10 carbon atoms to be studied.[3] A tapering effect is expected from the spectroscopic end, however, such that it is difficult to foresee chain lengths of greater than 15 carbon atoms being quantitated by ^{13}C NMR. This opens a window of opportunity for other analytical techniques (e.g., temperature-rising elution fractionation) to be used in conjunction with existing methods to yield a complete description of the branching state of a macromolecule.

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