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Using Solvents to Improve the Chemical Shift Differences Between Short-Chain Branch Methines and Long-Chain Branch Methines in Polyethylene Copolymers

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Summary: Detection and quantification of long-chain branches in some polyethylene copolymers is challenging due to the near coincidence of the chemical shifts for the carbons at the short-chain and long-chain branches present in these copolymers. The small chemical shift difference can be enhanced by changes in solvent and temperature. This allows one to use lower field magnets for some copolymers. Results are presented comparing several solvents and blends at a variety of temperatures using 500, 600 and 750 MHz spectrometers.

Keywords: branched; LLDPE; NMR; polyethylene (PE); solvent

Introduction

Ethylene-octene and ethylene-hexene copolymers are common linear low density polyethylene (LLDPE) polymers, representing over 75% of the total LLDPE market. As new materials are developed and commercialized for this growing market (6% global annual growth rate), it is expected that ethylene-octene and ethylene-hexene copolymers will continue to constitute a major portion of it. To fully evaluate these new materials, it is of critical value to expand and improve the available analytical methods for long-chain branching (LCB) analysis. Detection and quantification of LCB in these copolymers is challenging due to the near coincidence of the chemical shifts for the carbons at the short-chain branches (SCB) and long-chain branches present in these copolymers (Figure 1).

Solvent screening experiments have shown that solvent and temperature effects on the shift difference between the short and long-chain branch methines are quite significant. The small chemical shift difference observed in samples prepared using high boiling chlorinated aromatic solvents can be enhanced by changes in solvent and temperature. This allows one to use lower field magnets for some copolymers. A combination of resolution enhancement, solvent selection, sample temperature and high magnetic field (188 MHz, 150 MHz and 125 MHz ^{13}C) have been used to achieve enhanced resolution for the respective methine carbons of these two branch types. Quantification of LCB was validated by the measurement of a controlled sample that contained a known amount of long-chain branches.

This work is a continuation of the extensive application of NMR, rheology, and solution property methods to characterize polyolefins.[1] This capability will allow extended characterization of competitive copolymers and enhanced materials science understanding of new polyolefin materials.

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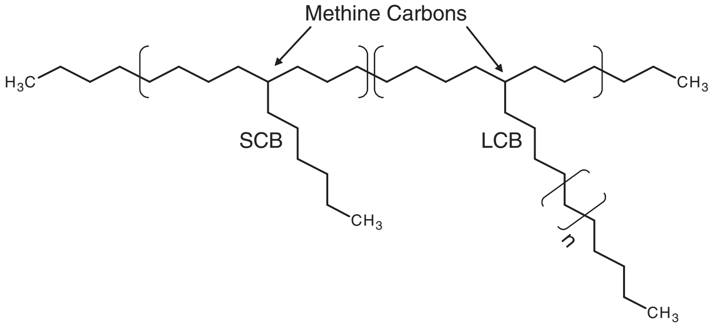

Figure 1.
Structure illustrating SCB and LCB methine carbons in an ethylene-octene (EO) copolymer.

Experimental Part

Sample Preparation

A total of 0.45 g of polymer is weighed into a 10 mm o.d. NMR tube. The solvent is added to the NMR tube. The tube is capped and placed in a heating block. The nominal temperature of the heating block is 150 °C. The hot sample is frequently mixed using a vortex mixer or a Buchi oven with rotating sample holder. The solvents used in this study are marginal polyethylene solvents; therefore preparation of a homogeneous sample is tedious. A significant amount of time and mixing is required to achieve solutions of sufficient homogeneity.

Sample Description

The total polymer weighed is a mixture of a linear low density ethylene-hexene or ethylene-octene copolymers and a long-chain branched homopolymer containing a known amount of branching. The various solvents used in this study are summarized in Table 1.

Data Acquisition

Nalorac high temperature 10 mm Z-spec probes were used at both 600 MHz and 750 MHz. Prior to data acquisition, the observed pulse widths are verified for both the ^{13}C and ^{1}H channels. Typical acquisition parameters for the Varian Inova 500 and 600 MHz and Varian Unity Plus 750 MHz NMR spectrometers are 64 K data file, 3.3 sec repetition rate and a 90° pulse width.

Data Processing

Chemical shift assignments are based on previously determined values of 30.0 ppm for the backbone methylene signal.[2,3] All data processing is done using NUTS (NMR Utility Transform Software) available from Acorn NMR.[4] The data files were processed with a weak Gaussian apodization function by setting $LB = -0.7$ Hz and $GF = 0.10$. This effectively changed the lineshape from Lorentzian to Gaussian without significant resolution enhancement except at the peak base.

Results and Discussion

The primary feature of interest when quantifying LCB in these copolymers is the separation between the LCB CH and the CH of the SCB associated with the EOE

Table 1.
Solvent compositions used in this study.

Name	Composition
TCE/ODCB	50/50 by weight 1,1,2,2-tetrachloroethane (TCE-d_2) and *o*-dichlorobenzene (ODCB).
Biphenyl	90/10 wt/wt biphenyl/biphenyl-d_{10}
Mesitylene	90/10 wt/wt 1,3,5 trimethyl benzene and 1,3,5 trimethyl benzene-d_{12}
Biphenyl/TCE	3.6/1 wt/wt biphenyl/TCE-d_2
Naphthalene	90/10 wt/wt naphthalene/naphthalene-d_8

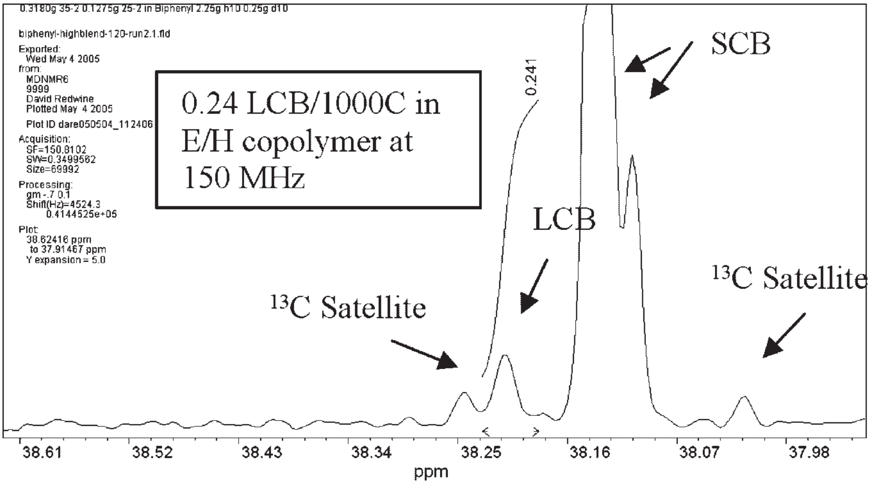

Figure 2.
A 150 MHZ ^{13}C spectrum of a sample containing a mixture of a linear ethylene-hexene copolymer and a long-chain branched HDPE. The LCB spike has a known level of 0.24 LCB per 1,000 total carbons.

or EHE triad. It is this chemical shift separation that has been adjusted by using various solvents in this work. It is also important to maintain some resolution between the LCB CH resonance and the ^{13}C satellite resonance of the SCB CH resonance. The optimum placement of the LCB methine signal is approximately 8.5 to 9 Hz down-field from the SCB CH resonance as shown in Figure 2 for an ethylene-hexene copolymer in biphenyl/TCE at 150 MHz ^{13}C. Using chlorinated aromatic solvents this degree of separation requires a magnetic field in excess of

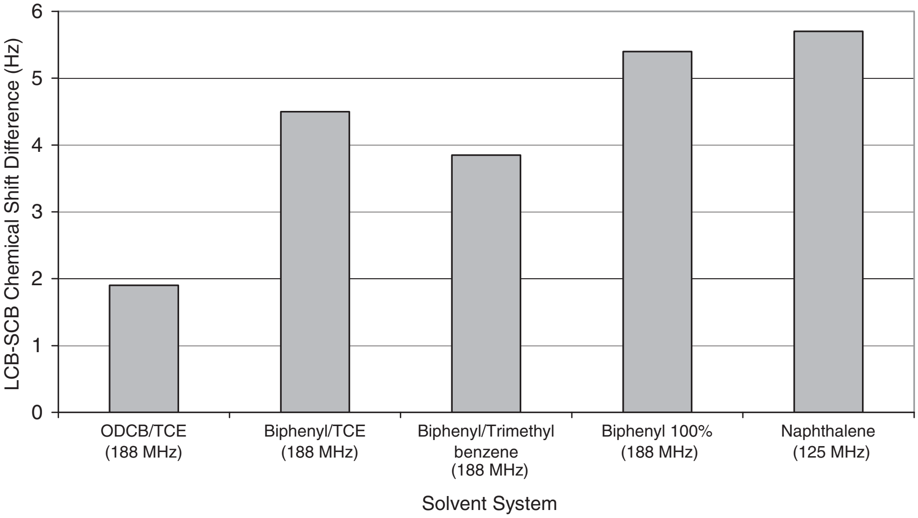

Figure 3.
A bar chart comparing the LCB-SCB methine separation at 120 °C for an ethylene-octene copolymer. The optimum solvent, naphthalene, gives a separation at 125 MHz which is over 2.5X the separation observed in the usual chlorinated solvent system at 188 MHz.

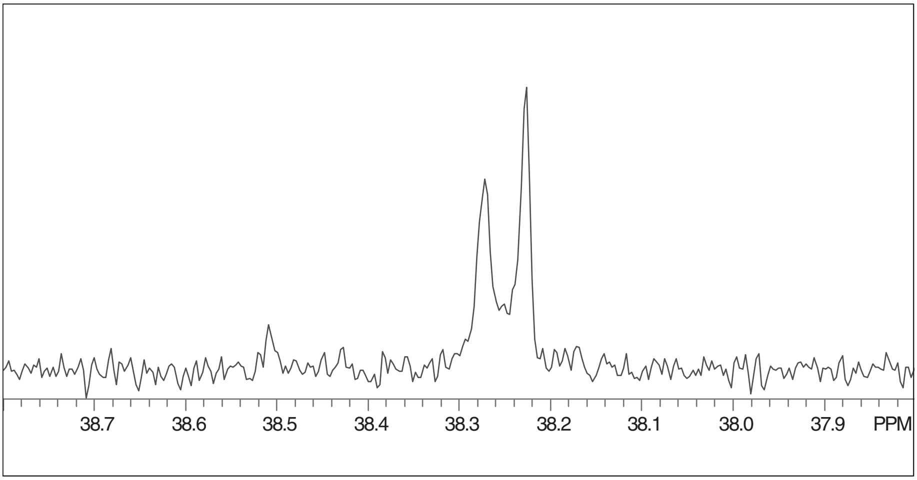

Figure 4.
A 125 MHZ ^{13}C spectrum of sample containing a mixture of a linear ethylene-octene copolymer and a long-chain branched HDPE. The LCB spike has a known level of 0.24 LCB per 1,000 total carbons. This spectrum was obtained in the optimum solvent, naphthalene, and shows a separation of 5.7 Hz.

750 MHz. A comparison of the LCB-SCB methine resonance separation is plotted in Figure 3. Figure 4 shows the resolved SCB and LCB methine signals for an EO copolymer.

Conclusions

The NMR methods described in this report produce ^{13}C spectra that satisfy the resolution and sensitivity requirements for LCB analysis in ethylene-hexene or ethylene-octene copolymers produced by transition metal polymerization. Dramatic shift enhancements have been observed for a variety of solvents using biphenyl and naphthalene as the primary solvents. Limited understanding of this effect is based on a rotational isomeric state conceptual model of the CH chemical shifts. The observed shifts for the SCB methine and the LCB methine are both average values over the population of the various rotomers possible for the main-chain and side-chain carbons near the methine carbon. Biphenyl and naphthalene produce a different population distribution and therefore result in different shifts compared to TCE/ODCB. It is believed that the differences occur mainly at the ends of the side-chains. These carbons are close enough to the side-chain end to give some selectivity in solvation for the SCB side-chain. This primary difference causes a secondary effect of changed steric effects at the CH carbon resulting in changes to the SCB and LCB methine resonance frequency.

Regardless of the mechanism at play we have succeeded in developing solvent systems which give the optimum separation of approximately 8.5–9 Hz for ethylene-hexene copolymers at 150 MHz ^{13}C (biphenyl/TCE), and ethylene-octene at 188 MHz ^{13}C (naphthalene).

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