

Melt-State ^{13}C MAS NMR Determination of Comonomer Type and Content in Ethylene/ α -Olefin Copolymers

Galen R. Hatfield* and William E. Killinger

Washington Research Center, W.R. Grace & Co.,-Conn. 7379 Route 32, Columbia, Maryland 21044

Robert C. Zeigler

Himont USA, a Montedison Company, R&D Center, 912 Appleton Road, Elkton, Maryland 21921

Melt-state ^{13}C NMR with magic angle spinning and dipolar decoupling is presented as an attractive method for the determination of comonomer type and content in polyolefins. The primary advantages of this approach are a decrease in analysis time and an ability to characterize samples not amenable to study by solution-state NMR. To illustrate this technique, five ethylene/ α -olefins are characterized including a sample that had been rendered insoluble due to cross-linking and one that had been formulated into an inorganic matrix. In all cases, the melt-state approach yielded comonomer contents in good agreement with those obtained via solution-state NMR.

Solution-state ^{13}C NMR is generally regarded as the only analytical technique capable of identifying and quantifying all of the branching features of a polyolefin. It is not surprising, then, that ^{13}C NMR studies of polyethylenes comprise a large body of published literature.¹ Various Raman,² IR,^{3,4} and thermal methods^{5,6} have been proposed to accomplish this same task. However, each of these suffers one or more major limitations including the lack of ability to differentiate between branch type, poor precision and accuracy, and low detection limits. Solution-state ^{13}C NMR suffers from none of these limitations. However, it does suffer from two notable problems. The first is the simple fact that the sample must be dissolved into an appropriate solvent. As a result, insoluble polyolefins such as those that have been electronically cross-linked, irradiated, or chemically modified are not amenable to this approach. A similar problem is encountered for polyolefins that have been formulated into a matrix containing an insoluble filler. Even in cases where the polymer is soluble, the postanalysis process of recovering an important experimental sample from a polymer/solvent gel is difficult, at best. The second problem with solution-state ^{13}C NMR is its relatively low sensitivity. The optimum concentration for analysis is 15 wt % polymer, and

problems with relaxation times require a minimum of 10-s pulse delays or the addition of paramagnetic relaxation agents.¹ As a result, overnight data acquisition times are common.

To circumvent these problems, we have begun obtaining high-resolution ^{13}C NMR spectra of polyolefins directly in the melt state with magic angle spinning and high-power dipolar decoupling. This experiment has only recently become feasible due to advances in NMR probe design which offer the ability to reach temperatures of up to 250 °C and to spin molten samples at speeds of 5–10 kHz. A preliminary report demonstrating the feasibility and operational details of this approach has been published elsewhere.⁷

In this paper we report on the use of melt-state MAS NMR to determine comonomer type and content in three common ethylene/ α -olefin copolymers. In addition, an irradiated copolymer and one that has been formulated into a filler matrix are characterized, illustrating how the use of this approach extends the power of NMR for characterizing polyolefins. We believe that this melt-state MAS NMR approach has important implications not only for polyolefins but for the study of other molten polymeric systems as well.

EXPERIMENTAL SECTION

Samples. The samples chosen for this study are copolymers of ethylene and 1-octene, 1-hexene, or 1-butene and are commercially available (Dow, Union Carbide, Exxon). The irradiated sample was pressed into a thin film and sequentially exposed three times to 85 kGy for 2 s (total exposure time of 6 s). The filled sample was mixed as a 50:50 blend with TiO_2 using a Brabender mixer at 50 rpm for 15 min at 180 °C.

NMR Spectroscopy. Solution-state ^{13}C NMR data were obtained at 100.6 MHz on either a Bruker DMX400 or a Bruker AM400. The acquisition conditions used were those prescribed^{1c} by proposed ASTM method X70-8605-2. Melt-state ^{13}C NMR data were obtained at 50.3 MHz on a Chemagnetics CMX200. Powdered samples were packed into ceramic rotors and spun at a speed of 3 kHz at the magic angle (MAS). The temperature of the sample was then elevated to 200 °C. Spectra were acquired in a fashion analogous to that described in proposed ASTM method X70-8605-2,^{1c} namely, using a single 90° pulse (4 μs) and a 10-s. acquisition delay. The primary differences were (1) the use of MAS and (2) the use of a high-power dipolar decoupling field.

- (1) See, for example: (a) Randall, J. *JMS-Rev. Macromol. Chem. Phys.* **1989**, C29, 201–313. (b) Cheng, H. N. *J. Appl. Polym. Sci.: Appl. Polym. Symp.* **1989**, 43, 129–163. (c) DePooter, M.; Smith, P. B.; Dohrer, K. K.; Bennett, K. F.; Meadows, M. D.; Smith, C. G.; Schouwenaars, H. P.; Geerards, R. A. *J. Appl. Polym. Sci.* **1991**, 42, 399–409.
- (2) Williams, K. P. *J. Polym. Commun.* **1984**, 25, 182–184.
- (3) Maddams, W. F.; Woolmington, J. *Makromol. Chem.* **1985**, 186, 1665–1670.
- (4) Usami, T.; Takayama, S. *Polym. J.* **1984**, 16, 731–738.
- (5) Burfield, D. R.; Kashiwa, N. *Makromol. Chem.* **1985**, 186, 2657–2662.
- (6) Adisson, E.; Ribeiro, M.; Deffieux, A.; Fontanille, M. *Polymer* **1992**, 33, 4337–4342.

(7) Zeigler, R. C. *Macromol. Symp.* **1994**, 86, 213–227.

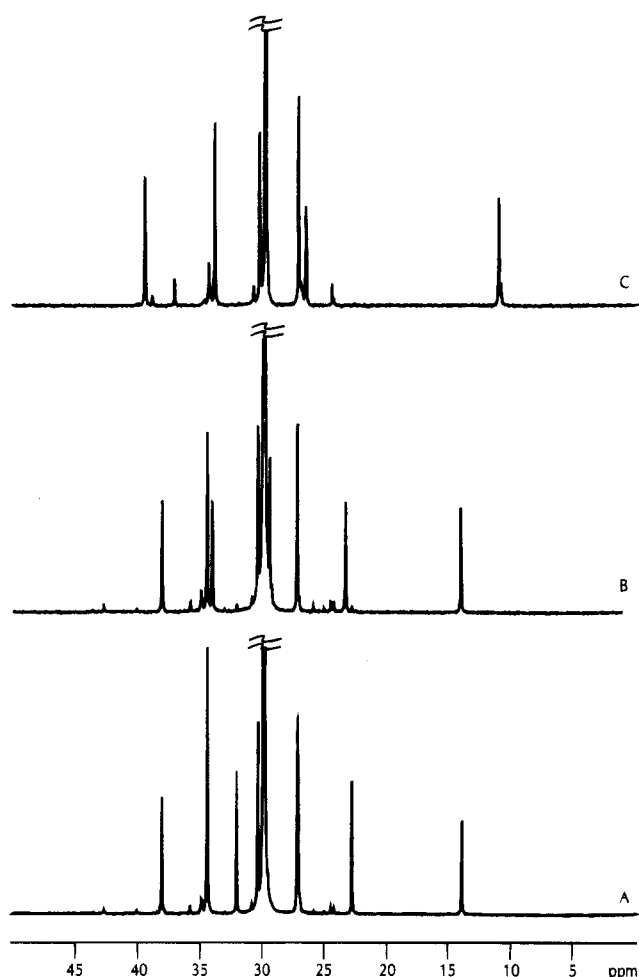


Figure 1. Solution-state ^{13}C NMR spectra of three ethylene/ α -olefin copolymers: (A) EO (sample I), (B) EH (sample II), and (C) EB (sample III).

RESULTS AND DISCUSSION

Ethylene/ α -olefin copolymers are a commercially important class of polyolefins. Of these, the most common include copolymers of ethylene (E) and 1-octene (O), 1-hexene (H), or 1-butene (B). Solution-state ^{13}C NMR studies of such systems comprise a large body of literature^{1,8} and form the basis for the work reported here.

Variable-Temperature Results. Given in Figure 1 are ^{13}C solution-state NMR spectra of three ethylene/ α -olefin copolymers in which the α -olefin is 1-octene (EO), 1-hexene (EH), or 1-butene (EB). These samples are identified in Table 1 as I–III, respectively. All three spectra are dominated by a large peak at 30 ppm which can be assigned to isolated methylene sequences. The other peaks in the spectrum ranging from 40 to 10 ppm arise from the short-chain branches incorporated into the polymer chain as a result of copolymerization with O, H, or B. Using the location and relative intensity of these peaks, it is possible to differentiate between the three comonomer types.^{1,8} For example, the EB copolymer gives rise to a methyl peak at 11 ppm while the EH and EO copolymers give rise to methyl peaks at 14 ppm. By integrating the NMR spectra, it is also possible to calculate comonomer content,^{1,8} and the solution-state ^{13}C NMR determined composition of samples I–III is given in Table 1.

(8) See, for example: (a) Hsieh, E.; Randall, J. *Macromolecules* **1982**, *15*, 353–360. (b) Hsieh, E.; Randall, J. *Macromolecules* **1982**, *15*, 1642.

The level of spectral resolution exhibited in Figure 1 is necessary to differentiate all of the ethylene/ α -olefin copolymer types. In addition, this level of resolution is necessary for determining comonomer content since all of the peaks shown in Figure 1 are integrated separately.¹ In contrast, given in Figure 2 are room-temperature solid-state ^{13}C MAS NMR spectra of the same three samples. As might be expected, note that the NMR line widths are much larger than those obtained in solution. This is largely due to restricted motion in the solid state. In addition, the spectra are also complicated by the fact that solid-state NMR differentiates between polyethylene segments that are in crystalline (34 ppm) and amorphous (32 ppm) environments.⁹ The combination of (1) spectral broadening, (2) morphological differences, and (3) varying spin–lattice relaxation times^{9,10} renders solid-state NMR ineffective at determining comonomer type and content.

Given in Figure 3 are high-temperature (200 °C) melt-state ^{13}C MAS NMR spectra of the same three copolymers. Note that these spectra have very nearly the same level of resolution as those typically obtained in solution (Figure 1). Changes in morphology and resolution can be seen to occur as a function of temperature in Figure 4. Note that most changes occur before 110 °C. This is reasonable since ethylene/ α -olefin copolymers in this compositional range typically melt in the region of 120 °C. For our studies, we chose a temperature of 200 °C simply to ensure that all of the crystallites had melted and that any potential thermal gradients in the NMR probe would not be an issue. For extended studies, however, temperatures closer to the melting point may be more attractive to avoid potential problems with oxidation or decomposition.

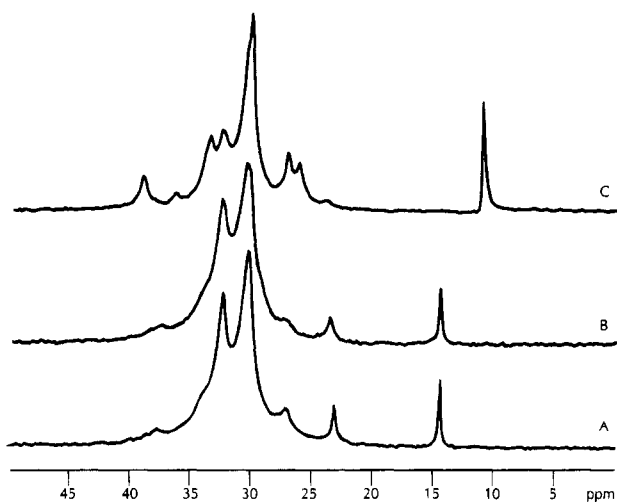
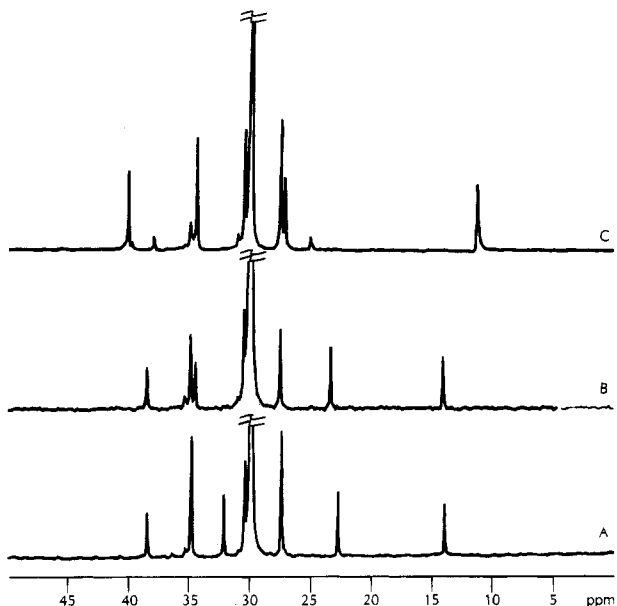
Quantitation. Prior to quantitation, it is necessary to understand and account for the spin–lattice relaxation behavior of the polymer in its melt state. Given in Table 2 are the spin–lattice relaxation times (T_1) for the principal carbons in samples I–III obtained under MAS conditions in the melt state. Since spin–lattice relaxation times are field dependent and since we are unable to carry out melt- and solution-state NMR experiments at the same field in our laboratories, we have chosen to compare our melt-state data against solution-state data obtained at the same field and published previously.^{1c} Note that in the melt state, T_1 's lengthen as the position on the side chain moves further from the polymer backbone. This same behavior has been mirrored in the solution state and has been extensively discussed elsewhere.^{1,8}

The relationships between temperature, line width, and spin–lattice relaxation times are complex and have been the subject of extensive study.^{10,11} We chose to use a temperature of 200 °C for three reasons: (1) the three polymers under study here have melting points around 120 °C, (2) since the temperature well exceeds the melting point, issues with thermal gradients should be minimized, and (3) the line widths had visually minimized to give spectra that were visually analogous to those obtained in the solution state. At this temperature, the relaxation values were close to those obtained in solution state, allowing us to quantitate

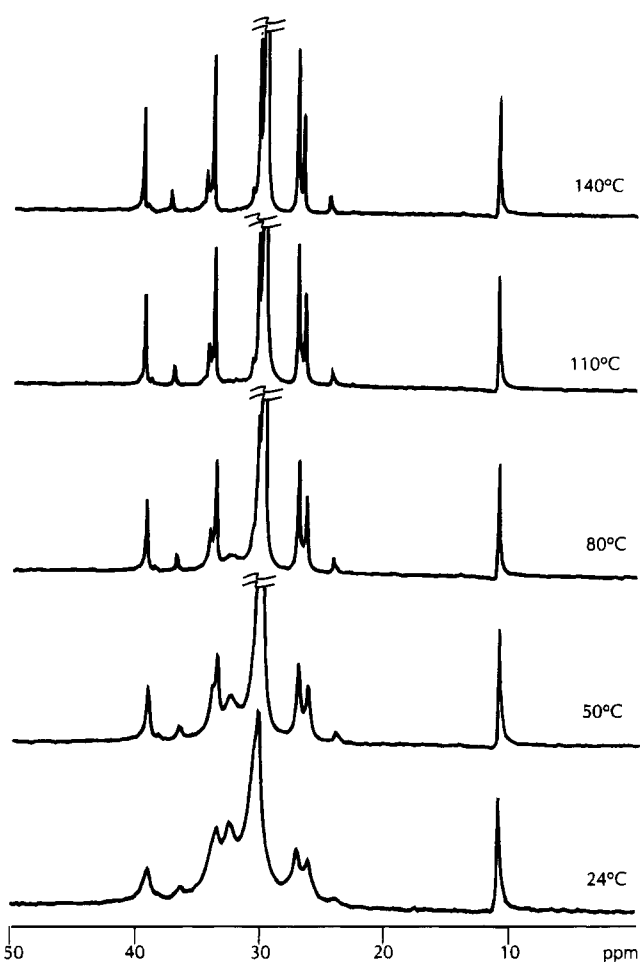
(9) Earl, W. L.; VanderHart, D. L. *Macromolecules* **1979**, *12*, 762–767.
 (10) See, for example: (a) Komoroski, R. A.; Makfield, J.; Sakaguchi, F.; Mandelkern, L. *Macromolecules* **1977**, *10*, 550–556. (b) Axelson, D. E.; Mathieu, P. J. *Polym. Sci.: Polym. Phys. Ed.* **1983**, *21*, 2319–2335.
 (11) See, for example: (a) Dechter, J. J.; Komoroski, R. A.; Axelson, D. E.; Mandelkern, L. J. *Polym. Sci.: Polym. Phys. Ed.* **1981**, *19*, 631–651. (b) Dekmejian, A.; Axelson, D. E.; Dechter, J. J.; Borah, B.; Mandelkern, L. J. *Polym. Sci.: Polym. Phys. Ed.* **1985**, *23*, 367–385.

Table 1. Sample Compositional Data

sample	comonomer	state	comonomer (mol %) determined by	
			solution-state NMR	melt-state MAS NMR
I	octene	powder	5.3	4.6
II	hexene	powder	3.9	3.4
III	butene	powder	11.5	11.0
IV	octene	pressed film irradiated at 85 kGy for 6-s	5.3	4.4
V	butene	formulated into a 50:50 blend with TiO ₂	4.2	4.1

**Figure 2.** Solid-state (30 °C) ¹³C NMR spectra of three ethylene/ α -olefin copolymers: (A) EO (sample I), (B) EH (sample II), and (C) EB (sample III).**Figure 3.** Melt-state (200 °C) ¹³C NMR spectra of three ethylene/ α -olefin copolymers: (A) EO (sample I), (B) EH (sample II), and (C) EB (sample III).

comonomer content using methods analogous to those previously reported.¹ Without repeating the details of this quantitative method, which is under ASTM review,^{1c} only select regions of peaks are chosen for quantitation based on their relaxation behavior and the use of a reasonable recycle delay. Using this approach and the melt-state data in Figure 3, we were able to obtain comonomer contents that are in good agreement with those obtained in the solution state. These are given in Table 1.

**Figure 4.** Solid-state ¹³C NMR spectra of sample III (EB) as a function of temperature.

Complex and Insoluble Systems. In order to demonstrate that the melt-state MAS NMR technique extends the ability of NMR, we have applied it to two additional systems. The first is a sample that was prepared by irradiating a pressed film of a standard resin with an electron beam dose of 85 kGy for 6 s. The irradiation process is known to induce cross-linking, which renders the sample insoluble and therefore not amenable to study by solution-state techniques. Given in Figure 5 is the melt-state ¹³C MAS NMR spectrum of the irradiated film. Note that the resolution is excellent and similar to that shown in Figure 3. As detailed in Table 1, integration of the data indicates a comonomer content that is in good agreement with the value obtained by standard solution-state NMR on the nonirradiated starting material.

As a second illustration, we analyzed a sample that had been mixed as a 50:50 blend with TiO₂ using a Brabender mixer at 50 rpm for 15 min at 180 °C. Although, by itself, the ethylene/ α -olefin copolymer in this sample is soluble, the presence of such

Table 2. Spin-Lattice Relaxation Times of the Predominant Carbons in EO, EH, and EB Copolymers Measured at 50 MHz^{a,b}

carbon type	EB copolymer		EH copolymer		EO copolymer	
	soln	melt	soln	melt	soln	melt
α	1.23	1.65	0.96	1.52	0.79	0.98
β	1.46	1.44	1.21	1.41	0.92	1.95
γ	1.51	1.75	1.36	2.03	1.22	1.42
$\delta\delta^+$	1.64	2.22	1.75	2.30	1.60	2.23
CH	1.91	2.53	1.48	1.97	1.06	1.29
6					0.79	0.98
5					1.30	1.95
4			1.19	1.52	na ^c	na
3			1.98	na	4.24	6.11
2	1.56	2.02	4.16	5.16	6.21	8.23
CH ₃	5.65	7.91	7.96	9.58	9.57	12.11

^a Solution-state data taken from ref 1c. ^b Melt-state data obtained in this study. ^c na, not available.

a high TiO₂ content would result in shimming difficulties. The ¹³C melt-state MAS NMR spectrum of this sample, given in Figure 5, shows a level of resolution and sensitivity approaching that given in Figure 3. Note, however, that the line widths of the NMR peaks are somewhat broader. This is presumably because the TiO₂ in this sample decreases the mobility of the molten polymer chains. However, this line width is still sufficient to provide quantitative data. As detailed in Table 1, integration of the data indicates a comonomer content that is in good agreement with value obtained by standard solution-state NMR on the nonformulated starting material.

Analysis Time. A comprehensive study of the differences in analysis time between solution- and melt-state NMR is beyond the scope of this work. However, several key points are worth noting at this time. The solution-state data are obtained on solutions that optimally contain 15% (by weight) polymer. By contrast, the melt-state data are obtained on the neat (100% by weight) polymer. All things being equal, this would increase the signal to noise (S/N) ratio by a factor greater than 6. However, solution-state experiments such as these are typically done using 10 mm probes while the melt-state experiments on our system use a 7.5 mm rotor, decreasing this gain by a factor just under 2. Considering only these two issues, we would expect the melt-

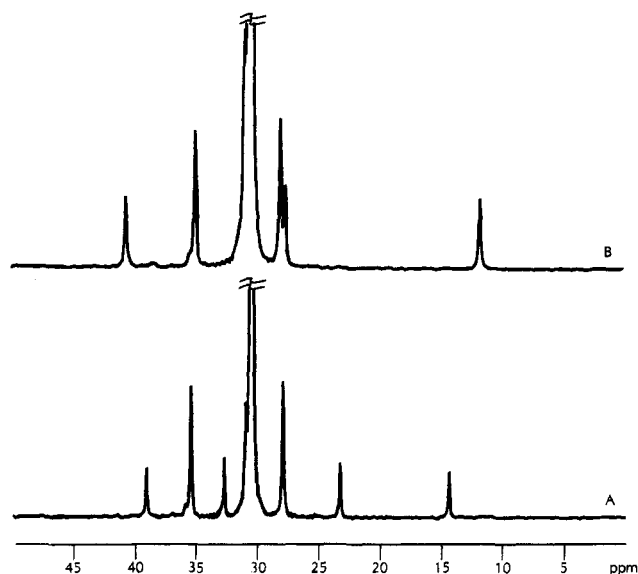


Figure 5. Melt-state (200 °C) ¹³C NMR spectra of (A) an irradiated ethylene/ α -olefin copolymer (sample IV, EO) and (B) an ethylene/ α -olefin copolymer formulated in a filler matrix (sample V, EB).

state experiment to have a S/N advantage of 3.75 or a net time savings of over 14. Such an expectation is clearly naive. One of the largest confounding factors is the void volume created while packing a rotor full of powder. Other differences such as field strength and rf coil performance also contribute to S/N differences. However, our empirical experience has shown that the melt-state approach offers a time savings advantage of typically at least 2–3 times that of solution-state NMR.

ACKNOWLEDGMENT

The authors thank E. Rakiewicz, Y. Guo (W.R. Grace, WRC), L. Freyer, and R. Stone (W.R. Grace, Cryovac) for technical discussions and sample support and J. Onuferko (W.R. Grace, WRC) for her continued support of this work.

Received for review February 28, 1995. [⊗] Accepted May 11, 1995.

AC950214C

[⊗] Abstract published in *Advance ACS Abstracts*, June 15, 1995.