NMR Study of Isolated 2,1-Inverse Insertion in Isotactic Polypropylene

Zhe Zhou,*,† James C. Stevens,† Jerzy Klosin,‡ Rainer Kümmerle,§ Xiaohua Qiu,‡ David Redwine,‡ Rongjuan Cong,† Angela Taha,† Jeff Mason,† Bill Winniford,† Paul Chauvel,† and Nikki Montañez||

Dow Chemical Company, Freeport, Texas 77541; Dow Chemical Company, Midland, Michigan 48667; Bruker BioSpin AG, CH-8117 Fällanden, Switzerland; and Kelly, Freeport, Texas 77541

Received December 11, 2008
Revised Manuscript Received January 22, 2009

Introduction

Isotactic polypropylene (iPP) contains stereo- and regio-errors that influence the polymeric properties as well as provide detailed insight into the mechanism of the polymerization catalyst. The vast majority of coordination catalysts for the stereoregular polymerization of propylene insert sequential monomer units in a head−tail fashion. Among these, the most common regio-error observed in polypropylene is an isolated 2,1-misinsertion which can exist in one of the four diastereoisomeric forms depending on the stereochemical relationship between the methyl groups. These four sequences labeled RE_1−RE_4 are shown in Figure 1 with 3D structures and Fisher projections.[1]

The most important method used for studying these microstructures is ^{13}C NMR. However, because of the low concentration of regio-errors (typically less than 1%) and the requirement of long acquisition times, relatively few detailed NMR studies have been undertaken.[2−9] These regio-errors studies were based mainly on additive ^{13}C chemical shift rules, model compounds, and calculations.

There are conflicting reports in the literature regarding the assignments of the carbon NMR spectrum as well as the stereochemistry of these regio-errors.[2−9] Asakura et al. characterized a highly regio-irregular homo-polypropylene containing about 40 mol % inverse insertion with 2D INADEQUATE[7,10,11] using a conventional probe. The S/N ratio of the reported spectrum was very low, which resulted in ambiguous results.[7] To address the sensitivity issue, a high-temperature cryoprobe was developed with S/N ratio about 5 times higher than that of conventional probes. With this cryoprobe, ^{13}C NMR with the desired S/N ratio can be acquired at much faster rates than previously possible. We used this cryoprobe to tackle the definitive assignment of low levels of regio- and stereoerrors in iPP using 2D INADEQUATE, allowing us to clarify any ambiguity in the literature.

Experimental Section

The iPP was synthesized in Dow Chemical Company. iPP (1−2 g) was added to a Wilmad 10 mm tube with 1−2 g of stock solvent and then purged in a N_2 box for 2 h. The stock solvent was made by dissolving 4 g of perdeuterated 1,4-dichlorobenzene in 39.2 g of *o*-dichlorobenzene. The tube was then heated in a heating block at 150 °C and then was repeatedly vortexed and heated. The tube was then left in the heating block for at least 24 h to achieve sample homogenization.

NMR experiments were carried out on a Bruker 400 MHz spectrometer with a 10 mm cryoprobe at 125 °C. The INADEQUATE was performed with the acquisition time of 0.41 s and pulse delay of 4.0 s. 320−384 transients per increment were acquired in a matrix of 4K (t_2) × 140 (t_1) data points. Waltz-64 decoupling sequence which we published recently was used.[12] Phase cycling was done according to Bourdonneau's method.[13] The data were processed with shifted sine bell weighting functions and zero filling to form a 4K × 1K matrix prior to Fourier transformation.

DEPT-135-HETCOR was run in phase-sensitive mode. 66 transients per increment were accumulated in a matrix of 4K (t_2) × 512 (t_1) data points. The HOESY experiments were performed with a mixing time of 0.4 s. 64 transients per increment were accumulated in a matrix of 2K (t_2) × 512 (t_1) data points.

Results and Discussion

We examined iPP prepared using representative procatalysts (Figure 2) **Cat1**[14] and **Cat2**,[15] as these catalysts cleanly produce iPP containing RE_1 and RE_2, RE_3 and RE_4, respectively, with few other complicating microstructures.

Figure 3A shows the 2D INADEQUATE of regio-error RE_1 in the iPP prepared with **Cat1**. We estimate that about 2.6 months of NMR instrument time would have been required to obtain a comparable 2D INADEQUATE spectrum with a conventional 10 mm BBO probe at 400 MHz. The carbon

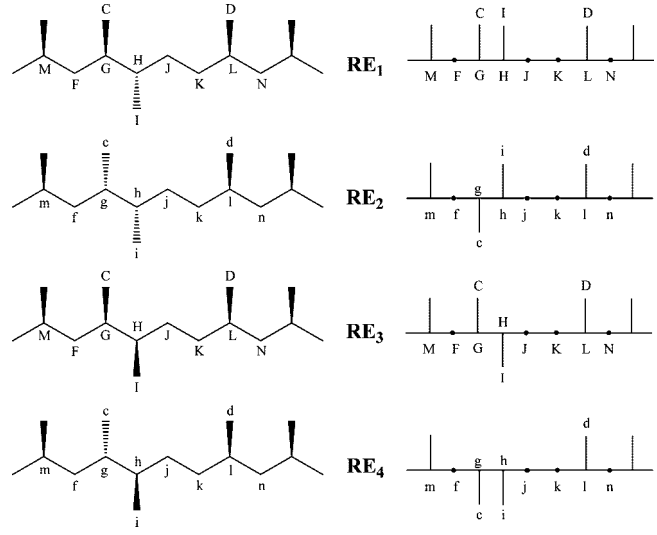

Figure 1. 3D structures and Fisher projections of 2,1-insertion regio-errors in iPP.

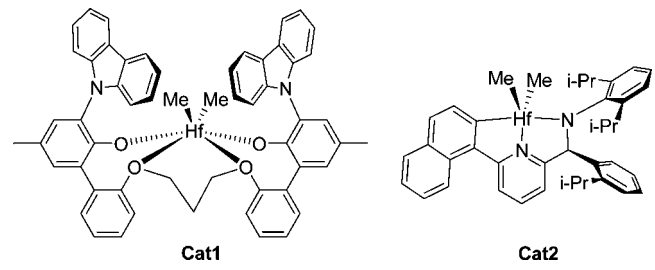

Figure 2. Structures of the procatalysts **Cat1** and **Cat2**.

* Corresponding author: Fax 1-979-238-0752; Tel 1-979-238-1387; e-mail zzhou@dow.com.
† Dow Chemical Company, Freeport, TX.
‡ Dow Chemical Company, Midland, MI.
§ Bruker BioSpin AG.
|| Kelly.

10.1021/ma802770f CCC: $40.75
Published on Web 02/19/2009

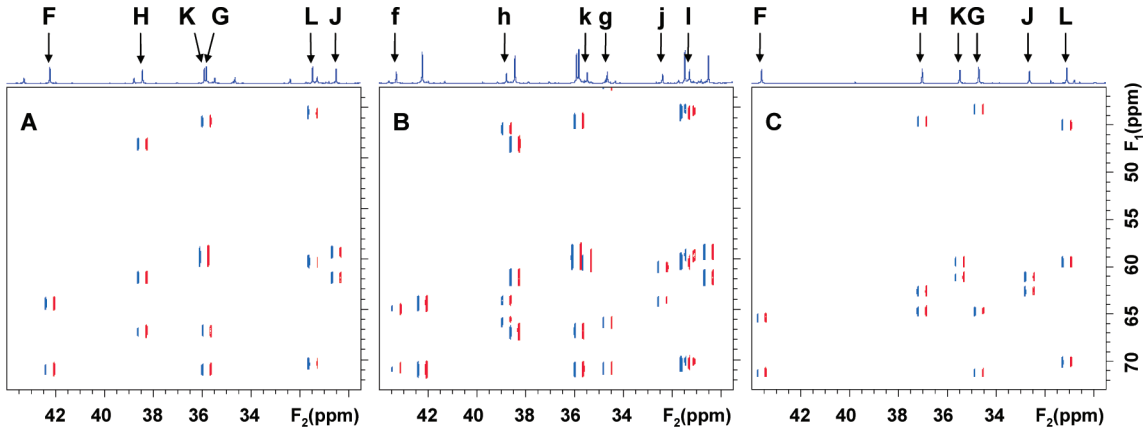

Figure 3. Fragments of 2D INADEQUATE. (A) 2,1-Insertion regio-errors (RE_1) in the iPP made with **Cat1**. (B) 2,1-Insertion regio-errors of the iPP made with **Cat1**. Only resonances for the regio-error with lower concentration (RE_2) are labeled. (C) 2,1-Insertion regio-error (RE_3) in the iPP made with **Cat2**. NMR time is 2−3 days.

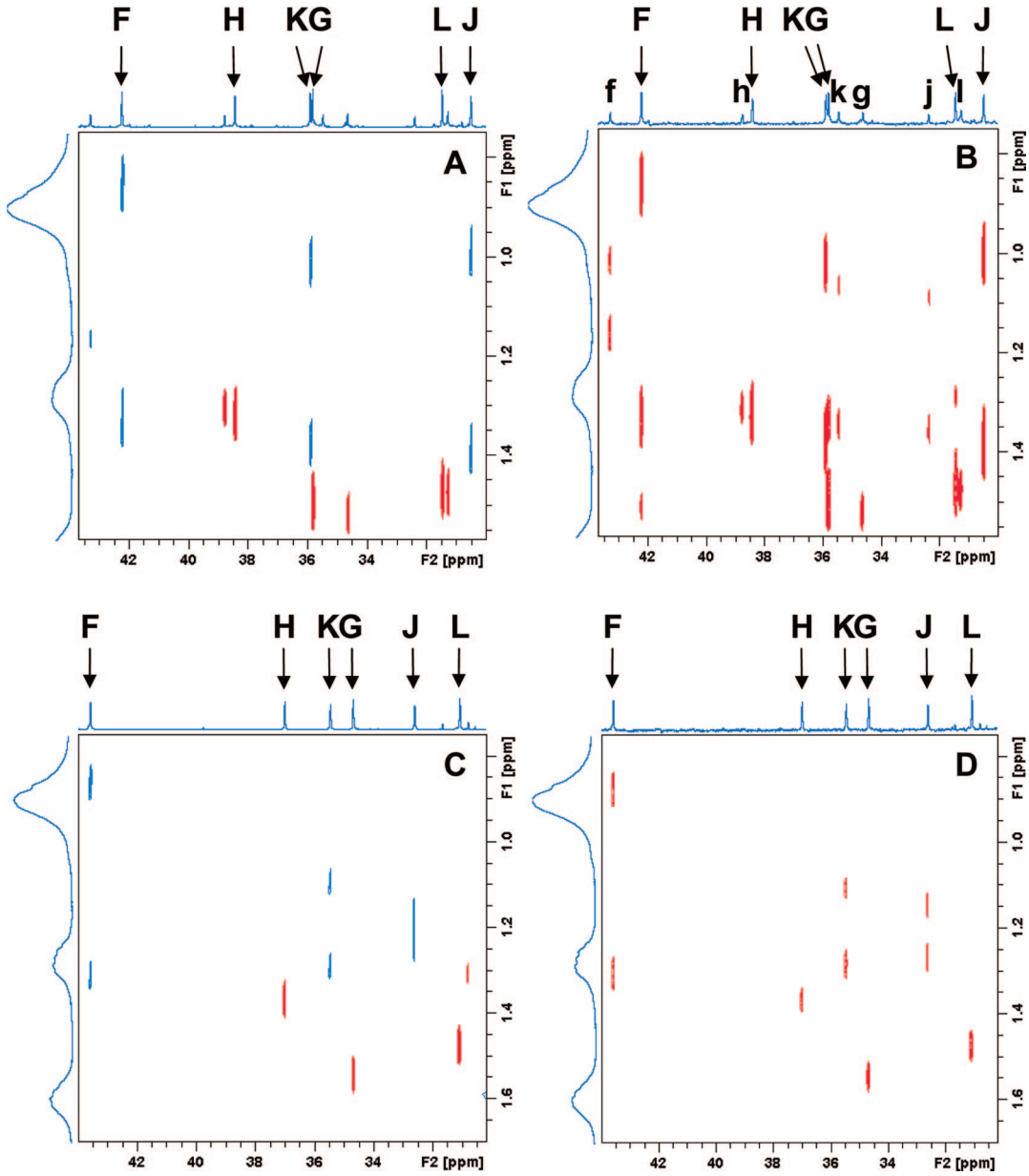

Figure 4. Fragment of DEPT-135-HETCOR and HOESY. Methyl and methine cross-peaks are red and methylene peaks are blue in DEPT-135-HETCOR. (A) DEPT-135-HETCOR of the iPP made with the **Cat1**. (B) HOESY of the iPP made with the **Cat1**. (C) DEPT-135-HETCOR of the iPP made with the **Cat2**. (D) HOESY of the iPP made with the **Cat2**.

Table 1. ^{13}C Chemical Shifts (ppm) of Regio-errors RE_1, RE_2, and RE_3 in iPP

regio-error	M	F/f	G/g	C/c	H/h	I/i	J/j	K/k	L/l	D	N
RE_1	29.29	42.22	35.81	17.63	38.43	17.26	30.50	35.90	31.46	21.12	46.05
RE_2		43.29	34.64	15.05	38.77	15.46	32.38	35.46	31.27		
RE_3		43.58	34.69	15.73	37.01	14.66	32.62	35.47	31.09	20.97	46.03

network is shown clearly in Figure 3A. The F_2 dimension is a regular 1D ^{13}C NMR with $^{13}C-^{13}C$ coupling. Since two coupled spins share the same double quantum frequency in the F_1 dimension, correlations are made by following horizontal traces parallel to F_2. Carbon connectivity is established by a sequence of vertical and horizontal steps. For example, starting with carbon J, it can be seen that carbon J is connected with carbon H; carbon H then connects to carbon G as seen in Figure 3A. Following this procedure, all the carbons near the inverted propylene unit in RE_1 are assigned. Some results are shown in the 1D NMR in Figure 3A (labels are described in Figure 1).

Lowering the display threshold in Figure 3A (Figure 3B) reveals the connectivity of the regio-error with lower concentration (RE_2). Some results are shown in the 1D NMR in Figure 3B. The level of RE_2 is only 0.4 mol %. It can be seen that the chemical shift sequences of c, i and l, j carbons in RE_2 are reversed compared with RE_1.

The 2D INADEQUATE of the iPP prepared with **Cat2** is shown in Figure 3C. The 2,1-insertion regio-error (RE_3) network is clearly shown in Figure 3C. The chemical shifts of the RE_1, RE_2, and RE_3 are summarized in Table 1.

Having established unambiguous carbon connectivity for these regio-errors, we then set out to independently obtain further evidence to confirm the stereochemical identity of RE_1, RE_2, and RE_3, using DEPT-135-HETCOR[16,17] and HOESY.[18] Figure 4A shows the DEPT-135-HETCOR of the iPP made with **Cat1**. The chemical shift difference of the two protons corresponding to peak F in Figure 4A is 0.48 ppm. It is well-known that the two diastereotopic methylene protons in iPP have different chemical shifts and the difference is about 0.41 ppm.[19] However, the two homotopic methylene protons in syndiotactic polypropylene have the same chemical shift.[19] This means that the signals labeled Figure 4A can only originate from either RE_1 or RE_3 (see the structures in Figure 1). It is difficult to know if the protons at position f (see Figure 4B) have a single peak or are split into two peaks from the DEPT-135-HETCOR (Figure 4A) because of the unusual cross-peak pattern. To determine the pattern of protons at f position for the iPP made with **Cat1**, an HOESY experiment was carried out (Figure 4B). Clearly, the two protons attached to the f carbon have different chemical shifts, but the difference is only 0.15 ppm, which is much smaller than that expected in regio-errors RE_1 and RE_3. This suggests that the resonances labeled with small letters in Figure 4B should originate from either RE_2 or RE_4.[9,19]

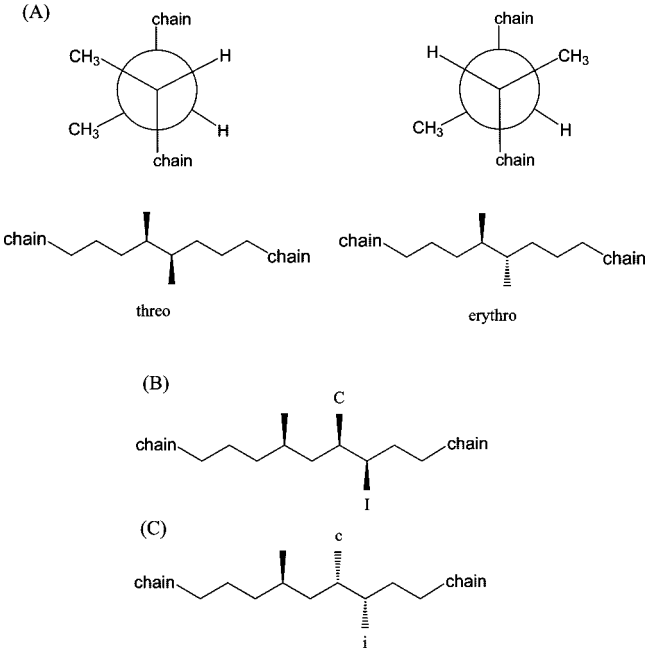

Figure 5. (A) Newman projections and 3D structures of polyethylene containing two H−H propylene units in the middle of the chain. (B, C) 3D structures of polyethylene containing three propylene units (T−H−H) in the middle of the chain.

For iPP prepared with **Cat2**, the chemical shift difference of the two protons corresponding to carbon F in DEPT-135-HETCOR (Figure 4C) is 0.45 ppm. The splitting for protons attached to carbon J could not be measured with DEPT-135-HETCOR (Figure 4C) and could be obtained using the HOESY (Figure 4D). It can be concluded that the signals labeled in Figure 4C can only originate from either RE_1 or RE_3 as the proton chemical difference corresponding to F carbon is quite large (see the structures in Figure 1).[9,19]

In order to further assign the structures established with DEPT-135-HETCOR and HOESY, the ^{13}C chemical shift prediction was used. The stereochemical relationship between the two methyl groups of head-to-head inserted propylene units can be either threo or erythro. Figure 5A shows the Newman projection of the two structures at their lowest energy state.

It is clear that each methyl carbon experiences two "gamma gauche" effects for the threo configuration and only one such effect in the erythro configuration. To estimate the "gamma gauche" effect, we compared the chemical shift of the methyl end group in polyethylene and the methyl group on the ethyl side chain in poly(ethylene-*co*-1-butene) which experiences such a "gamma gauche" effect. The change in chemical shift from 14.1 ppm for the former to 11.2 ppm for the latter shows that the "gamma gauche" effect for CH_3 is ~2.9 ppm upfield.[20] The chemical shifts of the methyl groups of the structures shown in Figure 5A can be estimated from the "gamma gauche" effect and the chemical shift for the methyl group in the EEPEE sequence which is at 20.0 ppm.[20] Thus, the two methyls for the threo stereoisomer should be around 14.2 ppm, and the methyls for the ethythro stereoisomer should be around 17.1 ppm. For the threo stereoisomer, if a methyl side chain is added to the β methylene as meso (*m*) configuration as shown in Figure 5B, the chemical shift for methyl C should move 0.8 ppm downfield similar to the chemical shift change for the methyl from EPE to PP(*m*)E.[21] On the other hand, for the threo stereoisomer, if we add a methyl side chain to the β methylene as racemic (*r*) configuration as shown in Figure 5C, the chemical shift for methyl c should not change much similar to the chemical shift change for the methyl from EPE to PP(*r*)E.[21] Therefore, the two structures identified with INADEQUATE with C/c close to 14−15 ppm can be assigned; the structure with C at 15.73 ppm is RE_3, and the structure with c at 15.05 ppm is RE_2 (Table 1). The difference between the C and c is 0.68 ppm, which is very close to the 0.8 ppm that we anticipated. The structure with a large proton chemical shift difference at the F position (Figure 4A) and the methyl groups shown at around 17.1 ppm in Table 1 is consistent with the RE_1. The

remaining unassigned regio-error in Figure 1 is RE_4. It is expected that the ^{13}C NMR resonances of the c and i methyl groups in the RE_4 should also appear around 17.1 ppm but with a small proton chemical shift difference at the f position (see the discussion above). The concentration of RE_4 in our sample is less than 0.04 mol %; we will report these assignments when higher concentration samples become available.

Our unambiguous results confirmed the assignments of RE_1 and RE_2 published in several papers and allowed us to assign two additional carbons of these regio-errors.[2,3,6] We can correct the misassignments of several previous reports concerning RE_2,[4,9] and we confirmed the prior assignments of RE_3 with additional assignments of carbon N.[15] The assignment of carbon N is critical in this analysis, as the splitting pattern of the two protons attached to the carbon N observed in the HOESY experiment can provide the information about the relative orientation of the two methyl carbons sandwiching the carbon N.

In conclusion, detailed 2,1-insertion regio-errors in iPP were studied with the help of 2D INADEQUATE. To our knowledge, this is the first conclusive and unambiguous experimental assignment of all of the carbons associated with these microstructures. Such microstructural characterization studies are important for developing polypropylene−ethylene copolymer NMR analysis method and for understanding the mechanism of the catalysts and the effects of low-probability structural features on the polymer physical properties.

Acknowledgment. We thank P. Hustad, G. Gobbi, D. Baugh, J. Potter, Y. He, D. Vanderlende, C. Li, A. Leugers, P. Ansems, K. Hool, M. Johnson, J. Adamson, R. Shick, C. Schmidt, and G. Marchand of Dow Chemical Company and J. DeCesare, M. Cool, P. Kostikin, and F. Haberle of Bruker BioSpin for their help on this project.

Supporting Information Available: INADEQUATE of the methyl region. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Natta, G.; Farina, M.; Peraldo, M. *J. Polym. Sci.* **1960**, *43*, 289.
(2) Tsutsui, T.; Ishimaru, N.; Mizuno, A.; Toyota, A.; Kashiwa, N. *Polymer* **1989**, *30*, 13150.
(3) Grassi, A.; Zambelli, A.; Resconi, L.; Albizzati, E.; Mazzocchi, R. *Macromolecules* **1988**, *21*, 617.
(4) Busico, V.; Cipullo, R.; Chadwich, J. C.; Modder, J. F.; Sudmeijer, O. *Macromolecules* **1994**, *27*, 7538.
(5) Asakura, T.; Demura, M. *Annu. Rep. NMR Spectrosc.* **1994**, *29*, 325.
(6) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253.
(7) Asakura, T.; Nakayama, N.; Demura, M.; Asano, A. *Macromolecules* **1992**, *25*, 4876.
(8) Cheng, H. N.; Ewen, J. A. *Makromol. Chem.* **1989**, *190*, 1931.
(9) Mizuno, A.; Tsutsui, T.; Kashiwa, N. *Polymer* **1992**, *33*, 254.
(10) Bax, A.; Freeman, R.; Frenkiel, T. A. *J. Am. Chem. Soc.* **1981**, *103*, 2102.
(11) Mattiello, D. L.; Freeman, R. *J. Magn. Reson.* **1998**, *135*, 514.
(12) Zhou, Z.; Kuemmerle, R.; Qiu, X.; Redwine, D.; Cong, R.; Taha, A.; Baugh, D.; Winniford, B. *J. Magn. Reson.* **2007**, *187*, 225.
(13) Bourdonneau, M.; Ancian, B. *J. Magn. Reson.* **1998**, *132*, 316.
(14) Boussie, T. R.; Brummer, O.; Diamond, G. M.; LaPointe, A. M.; Leclerc, M. K.; Micklatcher, C.; Sun, P.; Bei, X. U.S. Patent US 7241714, Symyx Technologies, Inc., 2007.
(15) Boussie, T. R.; Diamond, G. M.; Goh, C.; Hall, K. A.; LaPointe, A. M.; Leclerc, M. K.; Murphy, V.; Shoemaker, J. A. W.; Turner, H.; Rosen, R. K.; Stevens, J. C.; Alfano, F.; Busico, V.; Cipullo, R.; Talarico, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 3278.
(16) Bendall, M. R.; Pegg, D. T. *J. Magn. Reson.* **1983**, *53*, 144.
(17) Nakashima, T. T.; John, B. K.; McClung, R. E. D. *J. Magn. Reson.* **1984**, *59*, 124.
(18) Yu, C.; Levy, G. *J. Am. Chem. Soc.* **1984**, *106*, 6533.
(19) Busico, V.; Cipullo, R. *Prog. Polym. Sci.* **2001**, *26*, 443.
(20) De Pooter, 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.
(21) Cheng, H. N. *Macromolecules* **1984**, *17*, 1950.

MA802770F