

# A Carbon-13 NMR Study of Stereochemical Configuration in a Propylene-Ethylene Copolymer

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**ABSTRACT:** Natural-abundance carbon-13 NMR at 22.6 and 67.9 MHz has been used to study the stereochemical configuration in a low-ethylene content propylene-ethylene copolymer. No evidence was found for a mixture of meso and racemic configurations of the polypropylene chain across an inserted ethylene unit, a result consistent with the exercise of steric control by the asymmetric catalytic site.

Carbon-13 nuclear magnetic resonance (NMR) has been used with considerable success to study the stereochemical configuration of polypropylene<sup>1-9</sup> and copolymers of propylene and ethylene.<sup>1,9-16</sup> A substantial amount of information has been obtained about tacticity and the nature of steric defects in homopolymeric polypropylene. Insight into the mechanisms of steric control in Ziegler-Natta catalysis has been forthcoming from <sup>13</sup>C studies of propylene-ethylene copolymers.

We examine here a low-ethylene-content propylene-ethylene copolymer via natural abundance <sup>13</sup>C NMR at 22.63 and 67.90 MHz. Detailed information concerning the stereochemical configuration and sequence structure of the polymer has been obtained. The results greatly strengthen conclusions drawn from previous <sup>13</sup>C NMR work on the nature of steric control in stereospecific polymerization.

## Experimental Section

The propylene-ethylene copolymer examined here was the heptane-insoluble portion of a commercial resin (Diamond Shamrock Corp.) prepared using a Ziegler-Natta type catalyst. Carbon-13 NMR spectra were obtained at 120 °C and at 22.63 and 67.90 MHz on Bruker WH-90 and WH-270 FT NMR spectrometers, respectively. Solutions were 10–25% w/v in 4:1 *o*-dichlorobenzene:benzene-*d*<sub>6</sub>. Chemical shifts were measured with respect to internal hexamethyldisiloxane. Carbon-13 spin-lattice relaxation times (*T*<sub>1</sub>) and nuclear Overhauser enhancements (NOE) were measured using standard techniques.<sup>17,18</sup>

## Results and Discussion

The <sup>13</sup>C spectrum (22.63 MHz) of propylene-ethylene copolymer is shown in Figure 1. Chemical shift values relative to TMS are given in Table I. The spectrum essentially consists of three major resonances arising from the highly isotactic polypropylene segments of the polymer chains<sup>1-4</sup> plus a number of minor ethylene and propylene resonances. The minor resonances arise from the occurrence of a small percentage of randomly distributed ethylene units. No evidence was seen for sequences such as (CH<sub>2</sub>)<sub>2</sub> or (CH<sub>2</sub>)<sub>5</sub>.

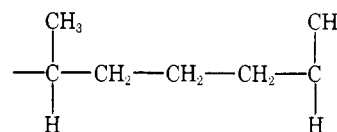
A number of previous assignments,<sup>9</sup> which were made using the Grant and Paul parameters<sup>19</sup> for a random copolymer of 20% ethylene content, have been confirmed on the basis of the results here for a low-ethylene-content copolymer. In the region of about 38 ppm (Figure 2A, ref 9) we are inclined to assign the upfield peak to carbons in position d (Table I) in the 20% ethylene copolymer. This is based on a comparison of the results for the 20% propylene-ethylene copolymer<sup>9</sup> and the results here, after "normalization" of the shift values. To accomplish this, peak k was assigned the same shift relative to TMS in both cases.

An interesting feature of the spectrum in Figure 1 is that the methyl groups at the ends of the pentadic unit centered on carbon l have been resolved from the main isotactic methyl resonance. That is, not only are the methyls (peak n) adjacent to the (CH<sub>2</sub>)<sub>3</sub> sequence resolved, but the next-nearest methyls (peak n') are resolved in addition. In a previous study<sup>15</sup> of a

propylene-ethylene copolymer prepared with a syndiospecific catalyst, the resolution of these next-nearest methyls from the main resonance was assumed, but not proven, to occur. On this basis, these authors<sup>15</sup> then drew conclusions concerning the mechanism of syndiotactic polymerization of propylene. From the spectral resolution obtained here for a highly isotactic copolymer, it can be concluded that their assumption was valid.

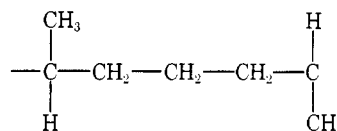
The <sup>13</sup>C *T*<sub>1</sub>'s and NOE's of the major isotactic polypropylene resonances were measured at 100 °C for a 10% solution in *o*-dichlorobenzene. The *T*<sub>1</sub> values of 0.86 s (CH<sub>2</sub>), 1.4 s (CH), and 2.0 s (CH<sub>3</sub>) are in agreement with those previously determined for isotactic<sup>2</sup> and atactic<sup>7</sup> polypropylene under comparable conditions. On the basis of previous *T*<sub>1</sub> work on atactic polypropylene<sup>7</sup> and linear<sup>2</sup> and branched<sup>20</sup> polyethylenes, it is not expected that the <sup>13</sup>C *T*<sub>1</sub>'s of the minor resonances will be over 2 s. The NOE's of all the major resonances were equal to 3, within experimental error (±0.2). This value agrees with that previously determined for isotactic polypropylene at 140 °C,<sup>2</sup> but not with that found for atactic polypropylene.<sup>7</sup> It was not possible to accurately measure the NOE's for the small resonances in Figure 1. It can be stated that these NOE's are large from a qualitative estimate of peak intensities in the gated decoupling experiment.<sup>18</sup> Thus, the spectrum in Figure 1 (Pulse delay = 6 s) is useable for approximate quantitative analysis. From the <sup>13</sup>C spectrum the ethylene content was estimated to be approximately 3 mol %.

A major question in stereospecific  $\alpha$ -olefin polymerization concerns the mechanism by which steric control of the polymerization process is exercised. In general, it is possible that steric control is exerted by the asymmetric catalytic site and/or by the last (asymmetric) unit of the growing polymer chain.<sup>21</sup> In a key study, Zambelli and co-workers<sup>10,11</sup> copolymerized propylene with low amounts of ethylene enriched in <sup>13</sup>C at one carbon. Several stereospecific catalysts were used. For the isotactic polymer, two additional resonances, of equal intensity and arising from the two types of methylene units (peaks d and l in Table I), were seen. Barring accidental coincidences of chemical shifts, this result is evidence that structures only of the type



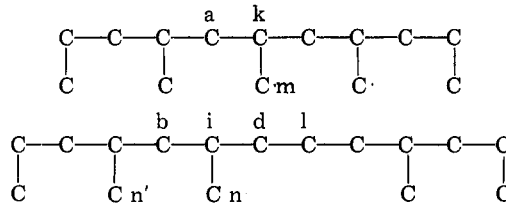
I

or only of the type



II

Table I  
<sup>13</sup>C Chemical Shifts of Propylene–Ethylene Copolymer

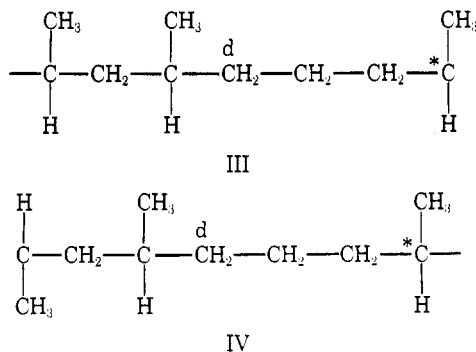
			
Position <sup>a</sup>	Shift <sup>b</sup>	Position <sup>a</sup>	Shift <sup>b</sup>
a	46.57	l	24.61
b	46.11	m	21.82
d	37.96	n'	21.61
i	30.99	n	20.90
k	28.96		

<sup>a</sup> Peak designations follow those used in ref 9 and 11. <sup>b</sup> In ppm relative to TMS. Estimated accuracy  $\pm 0.03$  ppm. Measured with respect to internal hexamethyldisiloxane (2.00 ppm) at 120 °C in 4:1 *o*-dichlorobenzene:benzene-*d*<sub>6</sub>. Polymer concentration = 10% w/v.

are present. Considering the isospecific nature of the catalyst used,<sup>10,11</sup> it was considered unlikely that only structure II was present. The presence of structure I along is strong evidence that steric control is exercised by the asymmetric catalytic site. If such control is exercised by the last monomer unit in the chain, a mixture of structures I and II would be expected in the copolymer. The latter situation would presumably yield two resonances each for sites d and l.

Two resonances attributed to structures analogous to I and II above were seen for carbon type d in the <sup>13</sup>C spectrum of propylene–ethylene copolymer synthesized using a syndiotactic catalyst (again, with enriched ethylene).<sup>11</sup> From this latter result, it was concluded that no accidental coincidences of chemical shift were present in the isotactic case. Only one resonance was seen for carbon type l in both cases.

However, there is some reason to question the evidence used to substantiate that no accidental coincidences of chemical shifts of the meso and racemic units have occurred in the isotactic polymer. The predominantly syndiotactic polymer investigated by Zambelli and co-workers<sup>11</sup> contained a substantial portion of isotactic placements (see Figure 1, ref 11) in addition to a relatively high concentration of sequences of the type [CH<sub>2</sub>CH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)CH<sub>2</sub>]. It is possible that the additional resonances seen in the <sup>13</sup>C spectrum of the above copolymer can be attributed to sensitivity of the d carbons to tacticity differences of directly adjacent polypropylene segments and not to structures of types I and II above. Structures III and IV illustrate this point. Such an effect



would be expected to be as important as a configurational change at the starred carbon across the ethylene unit, based on the number of intervening bonds.

On the other hand, Elgert and Ritter<sup>16</sup> have studied two alternating ethylene–propylene copolymers, via <sup>13</sup>C NMR.

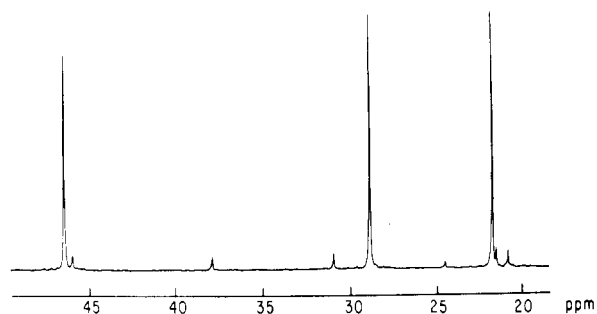


Figure 1. Proton-decoupled natural abundance <sup>13</sup>C FT NMR spectrum of propylene–ethylene copolymer (25% w/v in 4:1 *o*-dichlorobenzene:benzene-*d*<sub>6</sub>) at 120 °C and 22.6 MHz. Scale is in ppm from TMS. Spectral conditions: 779 transients; 3012 Hz spectral width accumulated in 8K points; 16K Fourier transform; 0.5 Hz artificial broadening due to sensitivity enhancement, 90° radiofrequency pulse width = 14.5  $\mu$ s.

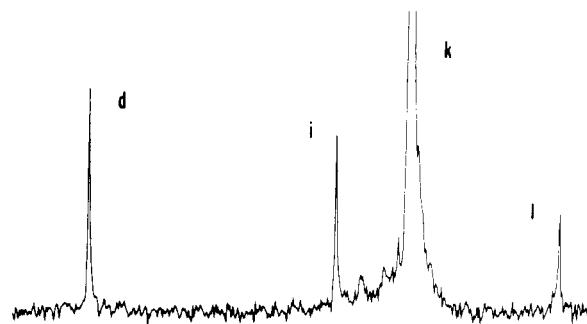


Figure 2. Expanded region of the 67.9-MHz <sup>13</sup>C NMR spectrum of propylene–ethylene copolymer at 120 °C. Peaks are labeled as in Table I.

One polymer, prepared by hydrogenation of 1,4-poly(1,3-pentadiene), had all units in the meso configuration, while the second polymer contained both meso and racemic units. The difference of the shift of the end CH<sub>2</sub> carbons in the (CH<sub>2</sub>)<sub>3</sub> sequences in meso and racemic units (most comparable to d here) was found to be only 0.05 ppm. This difference was barely resolvable at 90 MHz under the conditions reported. No discernible shift differences were seen for other carbons between meso and racemic units. It should be noted, however, that these spectra were obtained at 40–45 °C,<sup>16</sup> which is substantially lower than the temperatures typical of such studies. Presumably improved resolution of carbons in meso and racemic configurations would be obtained at 120 °C. In addition, the resonances of *meso*- and *racemic*-3,7-dimethylnonane could not be resolved at 22.6 MHz, and were barely resolvable at 55 MHz, as reported by Zambelli and co-workers.<sup>11</sup>

Lack of steric purity is not a problem for the propylene–ethylene copolymer examined here. The polypropylene chain segments are highly isotactic on the basis of previous work on isotactic polypropylenes.<sup>2,3,5</sup> The total amount of defects present can at most be several percent. As previously noted, the very low proportion of ethylene units is randomly distributed.

The spectrum at 22.6 MHz in Figure 1 clearly shows only one narrow resonance for each type of carbon in the vicinity of an ethylene unit. However, since it was necessary to utilize high magnetic field strengths to resolve resonances associated with meso and racemic configurations in the model compounds,<sup>11,16</sup> as mentioned above, we have examined our copolymer at 67.9 MHz and 120 °C. Figure 2 shows an expanded region of the 67.9 MHz of our propylene–ethylene copolymer. Only one resonance is seen for each carbon type under these

conditions. No indication of resonance broadening, which could be attributed to the presence of chemical shift non-equivalence, was apparent.

In light of this evidence, one must conclude that a mixture of meso and racemic configurations is not present and that the observed resonances can be attributed to only one type of structure (I or II above). In view of the isospecific nature of the catalyst employed, it is logical to assume that only structure I is present. Without suitable model studies, however, no absolute choice between I and II can be made. With the above-mentioned assumption in mind, our results here strongly support the conclusion that steric control is maintained by the asymmetric catalytic site, and not by the last unit of the growing polymer chain.

**Acknowledgments.** We thank Dr. Bruce Hawkins of Bruker Instruments, Inc., U.S.A., and Dr. David Axelson of Florida State University for obtaining 67.9-MHz  $^{13}\text{C}$  spectra of propylene-ethylene copolymer.

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## $^1\text{H}$ -NMR Studies of the 1,3-Dioxolan- $(\text{C}_2\text{H}_5)_3\text{O}^+\text{SbF}_6^-$ System. End Groups and Structure of the Active Species<sup>1</sup>

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**ABSTRACT:** The Fourier pulse transform (FPT)  $^1\text{H}$ -NMR method was used to study the structure of the growing macrocations in the polymerization of 1,3-dioxolan (1) and perdeuterated 1,3-dioxolan ( $1-d_6$ ) initiated with  $(\text{C}_2\text{H}_5)_3\text{O}^+\text{SbF}_6^-$  in  $\text{CD}_3\text{NO}_2$  solvent. Analysis of 300-MHz  $^1\text{H}$ -NMR spectra revealed that the  $(\text{C}_2\text{H}_5)_3\text{O}^+$  cation is quantitatively transformed during initiation into  $(\text{C}_2\text{H}_5)_2\text{O}$  and  $\text{C}_2\text{H}_5\text{-O-}$ ... polymer end group. No  $\text{C}_2\text{H}_5\text{-O}^+<$  cations, other than these from unreacted initiator, were detected; this fact indicates that the presence of the macrocyclic growing cations of the type  $\text{C}_2\text{H}_5\text{-O}^+<$  can be neglected. In the studies of the kinetics of cationation of 1,3-dioxolan with  $(\text{C}_2\text{H}_5)_3\text{O}^+\text{SbF}_6^-$  it was found that this reaction is slow ( $k_{\text{IM}} = 1 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1}$ , 35 °C,  $\text{CH}_3\text{NO}_2$  solvent) in comparison with propagation ( $k_{\text{p}} \sim 10^2 \text{ mol}^{-1} \text{ L s}^{-1}$  at the same conditions). This, however, does not influence the kinetics of  $(\text{C}_2\text{H}_5)_3\text{O}^+\text{SbF}_6^-$  disappearance because the rate constant ( $k_{\text{IP}}$ ) of the reaction of  $(\text{C}_2\text{H}_5)_3\text{O}^+\text{SbF}_6^-$  with dimethoxymethane used as a model of polymer segment is close to  $k_{\text{IM}}$  ( $k_{\text{IP}} = 0.95 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1}$ , 35 °C,  $\text{CH}_3\text{NO}_2$  solvent). Termination of the living poly-1,3-dioxolan- $d_6$  (after initiation is completed) with  $(\text{CH}_3)_3\text{N}$  gave predominantly linear macromolecules of the following structure:  $\text{CH}_3\text{CH}_2(\text{-OCD}_2\text{CD}_2\text{OCD}_2\text{-})_n\text{N}^+(\text{CH}_3)_3$ . Both end groups were identified in the FPT  $^1\text{H}$ -NMR spectra of the isolated polymers, the ratio of the end groups, determined from integration, being close to 1:1. Degrees of polymerization ( $\text{DP}_n$ ) calculated from end-group analysis were found to be close to the  $\text{DP}_n$  calculated for the living conditions assuming that one molecule of initiator gives one macromolecule.

It has been shown in our previous paper that poly-1,3-dioxolans (poly-1) prepared with stable oxocarbenium and trialkyloxonium cations as initiators ( $\text{C}_6\text{H}_5\text{CO}^+\text{SbF}_6^-$  and  $(\text{C}_2\text{H}_5)_3\text{O}^+\text{SbF}_6^-$ ) and terminated with  $\text{C}_2\text{H}_5\text{ONa}$ ,  $(\text{C}_6\text{H}_5)_3\text{P}$ ,  $(n\text{-C}_4\text{H}_9)_3\text{P}$ , and  $(\text{CH}_3)_3\text{N}$  are predominantly linear.<sup>2</sup> Macromolecules were found to contain two end groups, one coming from initiator and the second one from the terminating agent. Polymerization degrees ( $\text{DP}_n$ ) of these polymers are close to the calculated ones, i.e., to the ratio of concentration of reacted monomer to that of reacted initiator. This is what could be expected for a living system, like polymerization of tetrahydrofuran.<sup>3,4</sup>

On the other hand, poly-1 prepared with  $\text{HClO}_4$  had, according to Plesch,<sup>5,6</sup>  $\text{DP}_n$  rather independent of this ratio and dominated by transfer. These polymers were claimed to contain mostly cyclic macromolecules of low polymerization degrees. These findings were assumed as the basis of an idea of the "ring-expansion" growth of poly-1.<sup>5</sup>

However, in our opinion, neither linear nor cyclic structures of the isolated, killed macromolecules are straightforward arguments by themselves for the linear or cyclic growth of the living macromolecules.

Indeed, let us consider a general equilibrium between a cyclic and linear living poly-1: