Registry No. i-PP, 25085-53-4.

References and Notes

(1) Natta, G.; Peraldo, M.; Corradini, P. *Rend. Accad. Naz. Lincei* **1959**, *26*, 14.
(2) Natta, G.; Corradini, P. *Nuovo Cimento, Suppl.* **1960**, *15*, 40.
(3) Wyckoff, H. W. *J. Polym. Sci.* **1962**, *62*, 83.
(4) Gailey, J. A.; Ralston, P. H. *SPE Trans.* **1964**, *4*, 29.
(5) Turner-Jones, A.; Aizlewood, J. M.; Beckett, D. R. *Makromol. Chem.* **1964**, *75*, 134.
(6) Bodor, G.; Grell, M.; Kallo, A. *Faserforsch. Textil-Tech.* **1964**, *15*, 527.
(7) Miller, R. L. *Polymer* **1960**, *1*, 135.
(8) Zannetti, R.; Celotti, G.; Armigliato, A. *Eur. Polym. J.* **1970**, *6*, 879.
(9) Hosemann, R. *Acta Crystallogr.* **1951**, *4*, 520.
(10) McAllister, P. B.; Carter, T. J.; Hinde, R. M. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 49.
(11) Guerra, G.; Petraccone, V.; De Rosa, C.; Corradini, P. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 573.
(12) Addink, E. J.; Beintema, J. *Polymer* **1961**, *2*, 185.
(13) Corradini, P.; Petraccone, V.; Pirozzi, B. *Eur. Polym. J.* *1976*, *12*, 813.

---

^{13}C-Enriched End Groups of Polypropylene and Poly(1-butene) Prepared in the Presence of Bis(cyclopentadienyl)titanium Diphenyl and Methylalumoxane

Adolfo Zambelli,* Paolo Ammendola, Alfonso Grassi, Pasquale Longo, and Antonio Proto

Dipartimento di Fisica, Università di Salerno, 84100 Salerno, Italy. *Received May 20, 1986*

ABSTRACT: The stereochemical structure of ^{13}C-enriched end groups of isotactic polypropylene and poly(1-butene) prepared in the presence of bis(cyclopentadienyl)titanium diphenyl/methylalumoxane/^{13}C-enriched trialkylaluminum compounds is investigated by ^{13}C NMR analysis. The chain-end-controlled mechanism of isotactic-specific propagation is confirmed.

Propene and 1-butene have been polymerized at −60 °C in the presence of the homogeneous catalytic systems bis(cyclopentadienyl)titanium diphenyl/methylalumoxane/trimethylaluminum enriched with ^{13}C (CTP/MAO/TMA) and CTP/MAO/TEA (TEA = triethylaluminum enriched with ^{13}C on the methylene carbons). The polymers have been analyzed by ^{13}C NMR in order to check the mechanism of steric control and regiospecificity[1] by determining the stereochemical structure of the enriched end groups resulting from insertion of the monomers into the Mt–^{13}CH$_3$ or Mt^{13}CH$_2$–CH$_3$ bonds (Mt = metal atom of the catalytic complexes).

In a recent elegant paper, Ewen reported[2] that the above-quoted catalysts are partially isotactic specific and that the stereochemistry of the insertion of the monomer is controlled by the asymmetric configuration of the growing chain end (lk-1,3 asymmetric induction[2,3] replicating the configuration of the tertiary carbon of the growing chain end on the new asymmetric carbon resulting from the next insertion). The resonances of the natural-abundance carbons of polypropylene prepared in the presence of CTP/MAO/TMA (sample 1) and CTP/MAO/TEA (sample 2) (see Figure 1) are very similar to those already reported by Ewen,[2] and the analysis of the methyl stereochemical pentads[4] confirms that the stereochemical sequence of the propene units is in accord with the Bernoullian statistical model proposed by Bovey[5] with $P_{m\mathrm{P}} = 0.8_8$ and $P_{r\mathrm{P}} = 1 - P_{m\mathrm{P}}$ ($P_{m\mathrm{P}}$ and $P_{r\mathrm{P}}$ are the probabilities of isotactic (*m*) and syndiotactic (*r*) placements of the propylene units[6] (see Table I)).

The additional resonances observed in the spectrum of sample 1 at 20.4_8, 20.7_6, 21.4_1, and 21.7_3 ppm from HMDS (hexamethyldisiloxane) and in the spectrum of sample 2 at 27.4_2, 27.7_2, 28.4_1, and 28.6_7 ppm from HMDS are due, respectively, to the ^{13}C-enriched methyls of the isobutyl end groups and to the ^{13}C-enriched methylenes of the 2-methylbutyl end groups. The splitting of the resonances is due to the possible diastereotopic positions of the enriched carbons with respect to the methyl substituents of the second and third inserted propylene units (see Figure 2).

Table I
Enantioselectivity of Propagation and Initiation Steps

sample	monomer	AlR$_3$	P_m[a]	$I_{\delta\mathrm{t}}$[b]	$I_{\delta\mathrm{e}}$[b]
1	propene	Al(^{13}CH$_3$)$_3$	0.8_7	0.5	0.5
2	propene	Al(^{13}CH$_2$CH$_3$)$_3$	0.8_8	0.7	0.3
3	1-butene	Al(^{13}CH$_3$)$_3$	0.6_0	0.3	0.7
4	1-butene	Al(^{13}CH$_2$CH$_3$)$_3$	0.6_0	$\simeq$0.5	$\simeq$0.5

[a] P_m corresponds to $P_{m\mathrm{P}}$ or $P_{m\mathrm{B}}$, depending on the monomer (see text). [b] Probability of the indicated (δt or δe) placements evaluated from the relative areas of the resonances of the δt and δe enriched carbons ($I_{\delta\mathrm{t}}$ = {[δtζt] + [δtζe]}/{[δeζe] + [δeζt] + [δtζt] + [δtζe]}.

The resonances under consideration have been assigned in previous papers[1] to the enriched carbons (either methyl or methylene) having the stereochemical locations[8] δtζt, δtζe, δeζt, and δeζe at decreasing field (see Figure 2). The very presence of the resonances confirms, first of all, that the insertion of the monomer is primary (metal-to-C$_1$), at least for initiation and the two following propagation steps.[2] By considering the ratios between the areas of the resonances[10] of the enriched diastereotopic methyls of sample 1 ([δtζt]:[δeζe]:[δtζe]:[δeζt] = 1.0:1.0:0.15:0.15), one can visualize that insertion of propene on the Mt–^{13}CH$_3$ bond (initiation step) is not stereospecific. As discussed in ref 1, this conclusion comes from the fact that [δeζe] = [δtζt] and [δtζe] = [δeζt].

The fact that [δeζe]/[δeζt] = 6.7 shows that the insertion into the Mt–CH$_2$CH(CH$_3$)CH$_2$CH(CH$_3$)–^{13}CH$_3$ bond (second propagation step) is isotactic specific almost to the same extent as the following propagation steps. In fact (see Table I), it is also $P_{m\mathrm{P}}/P_{r\mathrm{P}} \cong 7$. On the other hand, one cannot say whether insertion into the Mt–CH$_2$CH(CH$_3$)–^{13}CH$_3$ bond (first propagation step) is stereospecific or not. From the relative areas of the resonances of the enriched methylenes of sample 2 ([δtζt]:[δeζe]:[δtζe]:[δeζt] = 1.0:0.4:0.2:0.05) and considering the insertion steps leading to these end groups, it may be seen that insertion

0024-9297/86/2219-2703$01.50/0 © 1986 American Chemical Society

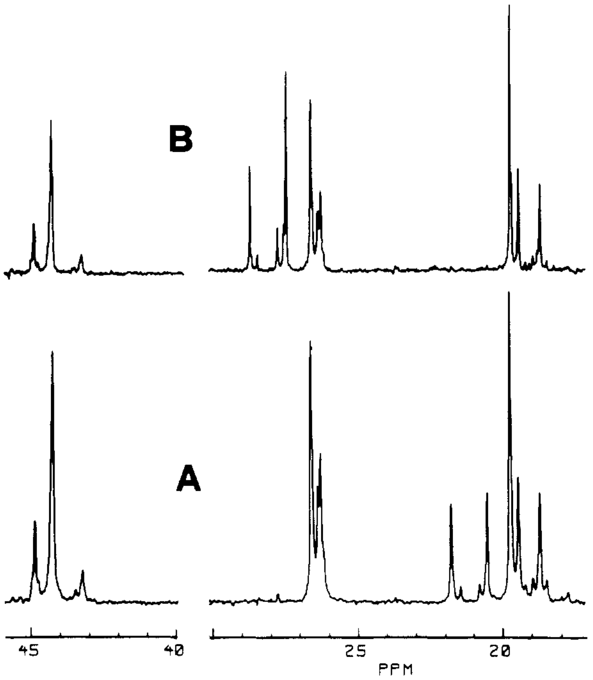


Figure 1. ^{13}C NMR spectra of sample 1 (A) and sample 2 (B). HMDS scale.

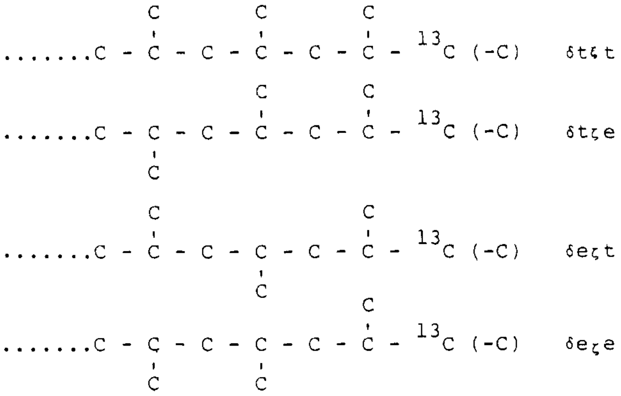


Figure 2. Fischer projection of diastereomeric $[7\text{-}^{13}C]$2,4,6-trimethylheptyl (octyl) end groups observed in polypropylene prepared by using the catalytic system CTP/MAO/TMA (TEA) enriched with ^{13}C. The diastereotopic placements of ^{13}C are indicated according to ref 8 by using Greek letters to denote the number of bonds between the enriched carbon and the methyl substituents along the backbone, followed by the symbols e (erythro) or t (threo), which give the steric relationship between the ^{13}C and the indicated methyl substituents.[8] A similar drawing (replacing methyl substituents with ethyl substituents) shows the diastereotopic position of the enriched carbon of the end groups of poly(1-butenes) 3 and 4. The same stereochemical notation is used for the enriched carbons of samples 3 and 4.

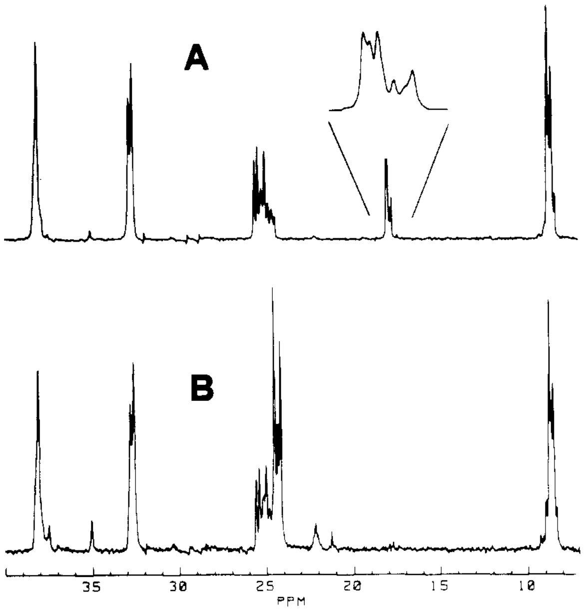


Figure 3. ^{13}C NMR spectra of sample 3 (A) and sample 4 (B). HMDS scale.

of propene into the Mt–$CH_2CH(CH_3)$–$^{13}CH_2CH_3$ bond (first propagation step) is almost as isotactic specific as all the other propagation steps: in fact, the probability of the δt placements of the enriched carbon ($I_{\delta t}$) is close to P_{mP} (see Table I).

One cannot say whether insertion into the Mt–$^{13}CH_2$–CH_3 bond (initiation step) is stereospecific or not.

The lack of information concerning the initiation step in sample 2 and the first propagation step in sample 1 precludes unequivocal conclusions concerning the mechanism of steric control. All of the information concerning enriched end groups of polypropylene considered up to now is consistent with the hypothesis that the stereochemistry of the addition is controlled by the chiral carbon of the growing chain end as well as with the hypothesis that the stereochemistry of the addition is controlled by chiral counterions,[11] provided that the alkyl group bonded to the metal of the catalytic complex is larger than CH_3. As reported previously,[1] the last hypothesis is correct for heterogeneous catalysts.

In Figure 3 are shown spectra of poly(1-butene) prepared in the presence of CTP/MAO/TMA (sample 3) and CTP/MAO/TEA (sample 4). The ^{13}C NMR spectrum of poly(1-butene) has already been assigned in the literature[12] and does not require further discussion. The only pertinent observation concerning natural-abundance carbons is that the relative areas of the resonances of the methylene stereochemical triads[12] (between 24.4_2 and 25.5_8 ppm) show that both samples of poly(1-butene) are appreciably less stereoregular than polypropylene. However, the sequence of the stereochemical triads (in fact, $(4[mm][rr])/[mr]^2 = (4 \times 0.36 \times 0.16)/0.48^2 = 1)$[12] is still in agreement with the same Bernoullian statistical model as polypropylene but $P_{mB} = 0.6$; see Table I. (P_{mB} is the probability of isotactic placements of the 1-butene units.) This fact suggests that in the presence of CTP the mechanism of steric control is the same for the polymerization of both propene and 1-butene. Assuming that the stereochemistry of the insertion is controlled by the asymmetric carbon of the growing chain end, one may understand the lower stereoregularity of poly(1-butene) on the basis that the steric requirements of the substituents of the chiral carbon (an ethyl group and the macroradical R) are more equal than in polypropylene (a methyl group and the macroradical R′) (Mt–$CH_2CH(C_2H_5)$–R, where R = $[CH_2CH(C_2H_5)]_n$; Mt–$CH_2CH(CH_3)$–R′, where R′ = $[CH_2CH(CH_3)]_n$).

This fact is somewhat diagnostic since when the insertion is controlled by asymmetric counterions (as happens in the presence of heterogeneous catalysts), the polymerizations of both propene and 1-butene are almost completely isotactic specific.[1] Even more diagnostic are the areas of the resonances occurring between 17.7_2 and 18.0_3 ppm from HMDS in the spectrum of sample 3 (Figure 3A). As reported in previous papers,[1] these resonances are due to ^{13}C-enriched $[2'\text{-}^{13}C]$2-methylbutyl end groups resulting from insertion of 1-butene into metal–$^{13}CH_3$ bonds (initiation step). The splitting of the resonances is due to the different possible stereochemical locations of the enriched carbon with respect to the ethyl substituents of the

Table II
Polymerization Conditions[a]

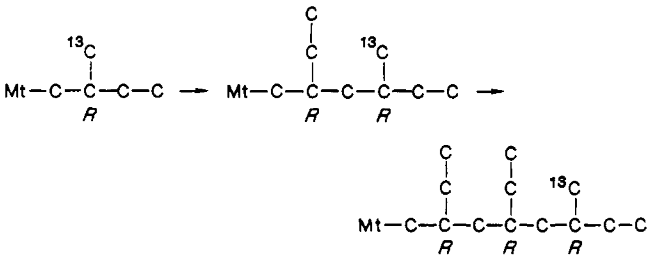
sample	monomer, mol	toluene, mL	CTP, mol	MAO,[b] g	TMA or TEA, mol	time, h	yield, g
1	0.1	45	1.5×10^{-5}	0.08	1.0×10^{-3}	2	0.1
2	0.2	40	6.0×10^{-5}	0.10	1.0×10^{-3}	24	0.3
3	0.5	30	7.5×10^{-5}	0.08	1.0×10^{-3}	48	2.0
4	0.6	20	6.0×10^{-5}	0.10	1.0×10^{-3}	27	0.1

[a] Temperature, −60 °C. [b] Added weight of methylalumoxane: See Experimental Section.

neighboring monomer units, analogous to the splitting observed for the enriched carbons of the end groups in samples 1 and 2. The assignment of these resonances is reported in a previous paper[1] (see also Experimental Section). Even though the resonances of the enriched methyls are not well separated, it can be readily observed that the area of the resonances of the δe enriched carbons of the end groups (between 17.9_4 and 18.0_3 ppm) is larger than that of the δt carbons (between 17.7_2 and 17.8_4 ppm). In addition, $I_{\delta e}$ (the probability of the δe placement of enriched carbons) is larger than $P_{m\mathrm{B}}$ (see Table I). This behavior in the initiation step is unique. In all previously observed polymers prepared in the presence of heterogeneous isotactic-specific catalysts and ^{13}C-enriched organometallic cocatalysts, $I_{\delta e} < I_{\delta t}$ and $I_{\delta e} \leq P_m$.

The most reasonable interpretation of these facts seems to be as follows: (1) the stereochemistry of the insertion of the first 1-butene (initiation) into Mt–$^{13}CH_3$ is not controlled; (2) the insertion into the metal– [2′-^{13}C]2-methylbutyl bond (first propagation step) is controlled by the configuration of chiral C-2; (3) the following insertions are controlled by the chiral carbon of the last unit entered into the chain.

In fact, one can see that three subsequent lk-1,3 inductions,[3] replicating the configuration (e.g., *R*) of the growing chain end (the isotopic substitution is not considered in assigning the absolute configuration of the asymmetric carbons)



just leads to end groups with the enriched methyl e with respect to the ethyls of the following butene units. As a consequence, the placement of the ethyl of the first inserted unit is t (or syndiotactic) with respect to that of the following one. The placement of the ethyl of the second unit is e (or isotactic) with respect to that of the third.

The fact that $I_{\delta e}$ is larger than $P_{m\mathrm{B}}$ implies that the nonbonded interactions of the substituents of the asymmetric carbon with the prochiral faces of the incoming monomer are more uneven for the 2-methylbutyl group (CH_3 vs. C_2H_5) than for any following one (C_2H_5 vs. $[CH_2CH(C_2H_5)]_n$–CH_3). The resonances of the enriched methylenes of the 2-ethylbutyl end groups of sample 4 overlap (see Figure 3B) with some of the resonances of the methylene stereochemical pentads. Since the stereoregularity of samples 3 and 4 is similar, the areas of the resonances of the enriched carbons can be roughly evaluated by difference between the spectra of samples 3 and 4. The difference spectrum (Figure 4) shows several resonances both in the region of the δt methylene carbons (centered at 24.2 ppm) and in that of the δe carbons (centered at 24.5 ppm). For the assignment, see the Experimental Section. Within the limitations of the accuracy of the measurement, we estimate that the areas of resonances of the two regions are equal. This is a corollary of the proposed mechanism of steric control. Accordingly, the stereochemistry of the two insertion steps

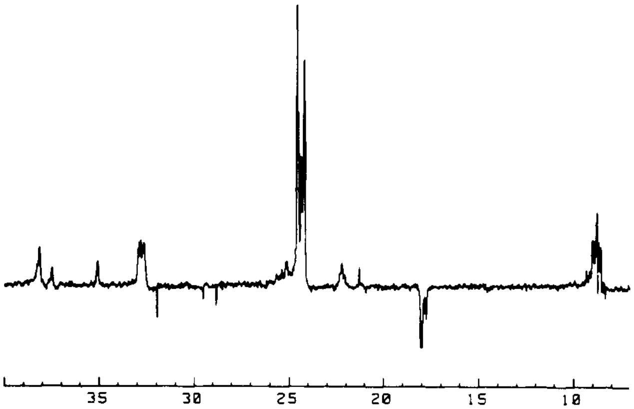


Figure 4. ^{13}C NMR difference spectrum between spectrum 3B and spectrum 3A. HMDS scale.

$$\mathrm{Mt{-}^{13}CH_2CH_3 \rightarrow Mt{-}CH_2CH(C_2H_5){-}^{13}CH_2CH_3 \rightarrow Mt{-}[CH_2CH(C_2H_5)]_2{-}^{13}CH_2CH_3}$$

cannot be controlled since no asymmetric carbon appears to be involved (excepting isotopic substitution, which is not expected to be relevant in view of asymmetric induction).

In conclusion, the stereochemical structure of the ^{13}C-enriched end groups fully corroborates the mechanism of isotactic steric control proposed by Ewen[2] for CTP/MAO. According to this author, this sort of isotactic steric control by the asymmetric chain end is associated with primary insertion.[2] It has been reported in the literature that the syndiotactic polymerization of propene in the presence of homogeneous catalysts based on vanadium salts and alkylaluminum halides involves steric control by the asymmetric carbon of the growing chain end (ul-1,3 induction), but that the insertion is secondary.[13] With the same catalyst, primary insertion leads predominantly to isotactic placements.[14]

According to Ewen, control by the asymmetric chain end can coexist with control by asymmetric counterions.[2] Perhaps such dual steric control could explain some results recently reported in the literature concerning the different stereospecificity of initiation steps for propene and 1-butene in the presence of certain heterogeneous catalysts.[15]

Experimental Section

Polymerization runs were performed at −60 °C (see Table II) in a stirred 100-mL flask under a nitrogen atmosphere by introducing in order (1) solvent, (2) MAO, (3) TMA or TEA, (4) monomer, and (5) CTP. Polymerization-grade C_3H_6 and C_4H_8, supplied by Società Ossigeno Napoli, were used without purification. Toluene was dried by boiling over metallic sodium and distilled under a nitrogen atmosphere. ^{13}C-Enriched (90%) $BaCO_3$

and CH_3I were supplied by Stohler Isotope Chemicals. Anhydrous $AlBr_3$ was supplied by Fluka A.G. and distilled. MAO was prepared as reported[2] by reaction of $Al(CH_3)_3$ and $CuSO_4{\cdot}5H_2O$ in toluene. The solvent and the unreacted $Al(CH_3)_3$ were removed by distillation under vacuum. CTP was prepared according to the literature.[16] $Al(^{13}CH_3)_3$ and $Al(^{13}CH_2CH_3)_3$ were prepared according to the following literature reactions[17-23] and distilled under vacuum:

$$\mathrm{^{13}CH_3I \xrightarrow{LiC_4H_9} {}^{13}CH_3Li \xrightarrow{AlBr_3} Al(^{13}CH_3)_3}\ \text{(60\% yield with respect to } \mathrm{^{13}CH_3I})$$

$$\mathrm{Ba^{13}CO_3 \xrightarrow{HClO_4} {}^{13}CO_2 \xrightarrow{MgCH_3I/H_2SO_4} CH_3{}^{13}COOH \xrightarrow{NaOH} CH_3{}^{13}COONa \xrightarrow{HCl\ +\ C_6H_5COCl} CH_3{}^{13}COCl \xrightarrow{LiAlH_4\ +\ (C_4H_9)_2O} CH_3{}^{13}CH_2OH \xrightarrow{PBr_2(C_6H_5)_3} CH_3{}^{13}CH_2Br \xrightarrow{Li} CH_3{}^{13}CH_2Li \xrightarrow{AlBr_3} Al(^{13}CH_2CH_3)_3}\ \text{(70\% yield with respect to } \mathrm{Ba^{13}CO_3})$$

After the polymerization was stopped by introducing methanol, the polymers were coagulated in acidified methanol and dried under vacuum. The NMR samples were prepared by dissolving in a 5-mm-o.d. tube ca. 100 mg of polymer in 0.8 mL of tetrachloroethane-*1,2*-d_2. Hexamethyldisiloxane was used as internal reference. All spectra were obtained on a Bruker WM-500 spectrometer operating at 125.77 MHz in the FT mode at a temperature of 393 K. The inverse-gated mode of recording was used in order to obtain proton-decoupled ^{13}C spectra without NOE. Most spectra are the result of 5K transients with 32K data points with an acquisition time of 1.5 s and a spectral width of 11 kHz. A pulse width of 9.0 μs, corresponding to a 73.6° flip angle, and a relaxation delay of 5 s were used. All spectra were processed with a 3-Hz line-broadening function prior to transformation. The resonances of the enriched carbons of the end groups of polypropylene in samples 1 and 2 were assigned by comparison with spectra reported in the literature for similar polymers[1]; the observed chemical shifts are not exactly the same as reported in the literature as a consequence of the different conditions used in recording the spectra. Similarly, the range of the chemical shift of the resonances of the diastereotopic enriched carbons of the end groups of polybutene samples 3 and 4 was determined by comparison with the spectra of similar polymers reported in the literature.[1,15]

Acknowledgment. Financial support by the Ministero della Pubblica Instruzione, CNR, Programma Finalizzato di Chimica Fine e Secondaria, is gratefully acknowledged. Dr. T. Tancredi is acknowledged for recording the ^{13}C NMR spectra.

Registry No. CTP, 1271-29-0; $H_3CCH{=}CH_2$, 115-07-1; $H_3CCH_2CH{=}CH_2$, 106-98-9; $Al(^{13}CH_3)_3$, 80480-38-2; $Al(^{13}CH_2CH_3)_3$, 80480-36-0; polypropylene, 25085-53-4; poly(1-butene), 9003-28-5.

References and Notes

(1) The same approach has been previously used for investigating stereospecific polymerization of 1-alkenes in the presence of heterogeneous catalytic systems. See, e.g.: Zambelli, A.; Sacchi, M. C.; Locatelli, P. Zannoni, G. *Macromolecules* **1982**, *15*, 211.

(2) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355.

(3) Seebach, D., Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1982**, *19*, 857.

(4) The resonances of the stereochemical methyl pentads have been entirely assigned in previous papers and therefore are not further discussed in this paper. See, e.g.; Zambelli, A.; Locatelli, P.; Bajo, G.; Bovey, F. A. *Macromolecules* **1975**, *8*, 687.

(5) Bovey, F. A.; Tiers, G. V. D. *J. Polym. Sci.* **1960**, *44*, 173.

(6) The stereochemical notation used in this paper is that of Frish et al.: Frish, H. L.; Mallows, C. L.; Bovey, F. A. *J. Chem. Phys.* **1966**, *45*, 1565.

(7) Also these resonances have been assigned in previous papers; see ref 1. Small deviations from the chemical shifts reported in ref 1 are due to the different conditions used in recording the spectra.

(8) Zambelli, A.; Locatelli, P.; Rigamonti, E. *Macromolecules* **1979**, *12*, 156.

(9) Zambelli, A.; Locatelli, P.; Sacchi, M. C.; Rigamonti, E. *Macromolecules* **1980**, *13*, 798.

(10) The areas of the resonances of the reported ^{13}C NMR spectra can be assumed to be proportional to the amounts of the different carbons since the spectra have been acquired in the inverse-gated mode to suppress the NOE. Hereinafter in this paper the stereochemical notations of Figure 2 will be used in square brackets in order to denote the relative concentrations of the enriched carbons of the end groups of each polymer (or the areas of the corresponding resonances).

(11) Shelden, R. A.; Fueno, T.; Tsunetsugu, T.; Furukawa, J. *J. Polym. Sci., Part A* **1965**, *3*, 23.

(12) The chemical shifts of the stereochemical pentads are not sufficiently resolved for a quantitative evaluation. The methylene triads (*mm* centered at 25.6 ppm, *mr* at 25.0 ppm, and *rr* at 24.6 ppm) are used for evaluating the statistical model for the stereospecific propagation. See, e.g.: Mauzac, M.; Vairon, J. P.; Sigwalt, P. *Polymer* **1977**, *18*, 1193.

(13) Zambelli, A.; Tosi, C., Sacchi, M. C. *Macromolecules* **1972**, *5*, 649.

(14) Zambelli, A.; Bajo, G.; Rigamonti, E. *Makromol. Chem.* **1978**, *179*, 1249.

(15) Locatelli, P.; Sacchi, M. C.; Tritto, I. *Macromolecules* **1986**, *19*, 305.

(16) Summers, L.; Uloth, R. H.; Holmes, A. *J. Am. Chem. Soc.* **1955**, *77*, 3604.

(17) Brown, T. L.; Rogers, M. T. *J. Am. Chem. Soc.* **1957**, *79*, 1859.

(18) Curtin, D. Y.; Tveten, J.. L. *J. Org. Chem.* **1961**, *26*, 1764.

(19) Murray, A.; Williams, D. L. In *Organic Synthesis with Isotopes*; Interscience: New York, 1959; p 34.

(20) Ankher, H. S. *J. Biol. Chem.* **1948**, *176*, 1333.

(21) Cox, J. D.; Turner, H. S. *J. Chem. Soc.* **1950**, 3176.

(22) Horner, L.; Oediger, H.; Hoffman, H. *Justus Liebigs Ann. Chem.* **1959**, 626, 26.

(23) Bryce-Smith, D.; Turner, E. E. *J. Chem. Soc.* **1953**, 861.