(6) R. J. Wittebort and A. Szabo, *J. Chem. Phys.*, **69**, 1722 (1978).
(7) T. Yasukawa, D. Ghesquiere, and C. Chachaty, *Chem. Phys. Lett.*, **45**, 279 (1977).
(8) A. Tsutsumi, *Mol. Phys.*, **37**, 111 (1979).
(9) D. Ghesquiere, C. Chachaty, Buu Ban, and C. Loucheux, *Makromol. Chem.*, **177**, 1601 (1976).
(10) A. Tsutsumi and C. Chachaty, *Macromolecules*, in press.
(11) D. Ghesquiere, Buu Ban, and C. Chachaty, *Macromolecules*, **10**, 743 (1977).
(12) D. Ghesquiere and C. Chachaty, *Macromolecules*, **11**, 246 (1978).
(13) D. Doddrell, V. Glushko, and A. Allerhand, *J. Chem. Phys.*, **56**, 3683 (1972).
(14) R. M. Fuoss and J. G. Kirkwood, *J. Am. Chem. Soc.*, **63**, 385 (1941).
(15) K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 329 (1941).
(16) T. M. Connor, *Trans. Faraday Soc.*, **60**, 1574 (1964).
(17) T. Yasukawa and C. Chachaty, *Chem. Phys. Lett.*, **43**, 565 (1976).
(18) C. Rerat, *Acta Crystallogr.*, **15**, 427 (1962).
(19) A. Tsutsumi, J. P. Quaegebeur, and C. Chachaty, *Mol. Phys.*, in press.

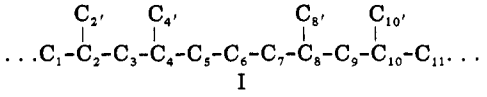
Ethylene–Propylene Copolymers and Mechanism of Steric Control

A. Zambelli,* M. C. Sacchi, and P. Locatelli

Istituto di Chimica delle Macromolecole del C.N.R., 20133 Milano, Italy.
Received March 5, 1979

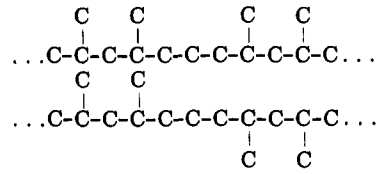
ABSTRACT: The high-resolution ^{13}C NMR spectra of a sample of isotactic ^{13}C-enriched ethylene–propylene copolymer and of 2,4,8,10-tetramethylundecane are compared. The previous conclusions concerning the unique stereochemical placement of isolated ethylene units in isotactic copolymers and the mechanism of the isotactic steric control are confirmed.

In a recent paper,[1] conformational differences among the various propylene stereosequences were utilized for predicting the ^{13}C NMR chemical shifts of the carbons (labeled 5, 6, 7 in I below) of the ethylene–propylene copolymers containing isolated ethylene units flanked by long head-to-tail propylene sequences:



I

The predicted shifts[1] were in agreement with those previously measured in model compounds[2] except for the influence of the relative configuration of C_4 and C_8 on the chemical shift of the C_5–C_7 pair and of C_6. For instance, according to ref 1, the shift difference between the methylene carbons concerned in the stereosequences here drawn in Fisher projection



(called $T^mmE^mmT^m$ and $T^mmE^rmT^m$ in ref 1 and ++,++ and ++,−− in ref 2) should be undetectable. On the contrary, according to ref 2, at least the difference between the chemical shifts of the C_5–C_7 pairs would be detected.

The argument is by no means irrelevant because it involves the conclusions, exactly opposite in ref 1 and 2, concerning the suitability of the ^{13}C NMR analysis of ethylene–propylene copolymers in order to establish the mechanism of the steric control in isotactic specific polymerization of α-olefins.

On this subject, it may be of some use to compare the spectra of 2,4,8,10-tetramethylundecane (TMU) and of a copolymer of 90% enriched $^{13}CH_2{=}CH_2$ (0.05 mol %) with natural abundance propylene (99.95 mol %), prepared in the presence of the highly isotactic-specific catalyst system ARA $TiCl_3$–$Al(C_2H_5)_2I$[3] (Figure 1A,B).

TMU has been chosen for comparison because it comprises only two asymmetric carbons, so that splitting of the resonance of the C_5–C_7 pair can arise only from the relative configuration of C_4 and C_8 and because it is a more realistic model of the copolymer than 3,7-dimethylnonane (DMN), reported in a previous pioneering paper.[4]

In Figure 1A it may be observed that only one unsplit resonance is observed for C_6 of TMU while two resonances ($\Delta\nu$ = 0.04 ppm) are observed for the C_5–C_7 pairs in meso and racemic TMU (see expanded spectra).

In the spectrum of the copolymer, the completely isotactic arrangement of the propylene units can be appreciated (methyl, methylene, and methine resonances at 19.7_9,44.5_9, and 27.0_0 ppm, respectively). In addition, only two sharp resonances of the same intensity and of the same half-height width are observed for the C_5–C_7 pair and for C_6 (the equal intensity is due to the selective enrichment of $^{13}CH_2{=}CH_2$).

The resonances observed in the spectrum of the copolymer for C_5–C_7 and C_6 are wider than those observed in the spectrum of TMU, but a splitting such as that observed for the C_5–C_7 pair in meso and racemic TMU should still be easily detected also in the copolymer, at least as a broadening of the resonance at 35.9_2 ppm in comparison with that at $22,5_0$. Such a splitting has never been observed by us even by artificially reducing the width of the signals by multiplication of the FID with a suitable triangular function or by Sanders and Komoroski, who previously observed isotactic ethylene–propylene copolymers at higher magnetic field.[5]

In addition, an increasing splitting has been observed between the resonances of C_4–C_6 pairs in meso and racemic DMN ($\nu_r - \nu_m$ = −0.03 ppm)[6] and the resonances in C_5–C_7 pairs in meso and racemic TMU ($\nu_r - \nu_m$ = +0.04 ppm).

Therefore, we expect that in the spectrum of the isotactic copolymer, provided that more than one unique configurational stereosequence, including substituted

0024-9297/79/2212-0783$01.00/0

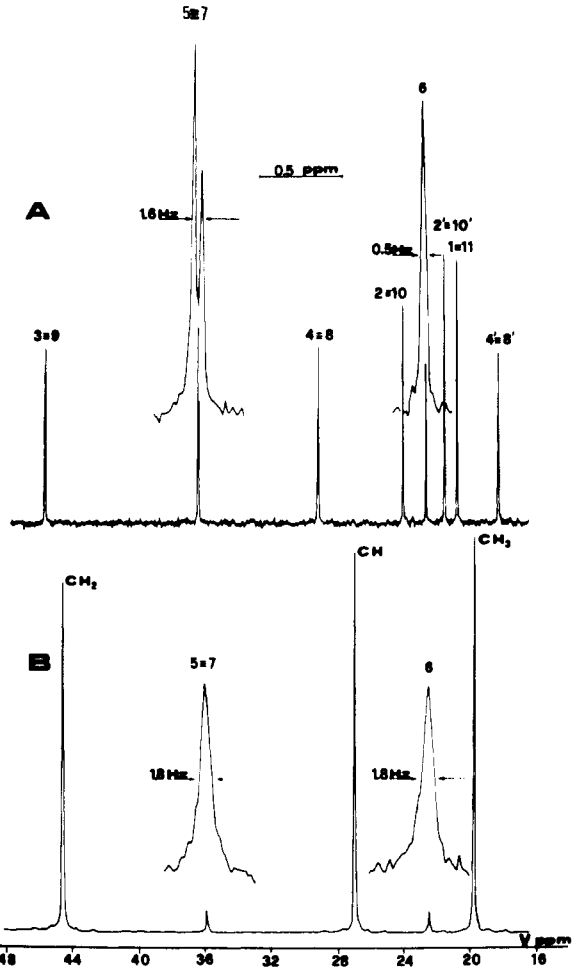


Figure 1. ^{13}C NMR spectra of (A) 2,4,8,10-tetramethylundecane (TMU) and (B) the 1-^{13}C-ethylene–propylene isotactic copolymer. Tenfold expansions of the resonances of C_5–C_7 and C_6 are also shown. Resonance peaks are numbered according to structure I.

carbons C_4 and C_7, were present around the C_5–C_6–C_7 methylene carbon sequence, there would be observed at least the same splitting as in TMU.

Consequently, our conclusion is that ^{13}C NMR analysis of ethylene–propylene copolymers is an adequate method for studying the mechanism of steric control in α-olefin polymerization, provided that due attention is paid to the observation of suitable model compounds[2] and the now available instrumental resolution is realized.

Experimental Section

TMU was synthesized as previously described[2] starting from partially resolved 1-chloro-2,4-dimethylpentane.

The ethylene–propylene copolymer was prepared as follows:[4] in a reaction vessel equipped with a magnetic stirrer, thermostated at 15 °C, were introduced under a nitrogen atmosphere 20 mL of anhydrous *n*-heptane, 1.5 g of $TiCl_3$ (ARA Stauffer), and 2 mL of $Al(C_2H_5)_2I$. Nitrogen was removed by vacuum pump, and H_2 was introduced up to 0.6 atm. Atmospheric pressure was restored by rapidly introducing a mixture of propylene and 1-^{13}C-ethylene (0.015 mol % of 90% enriched ethylene). The reaction was carried out for 1 h, and the pressure was kept constant by introducing, as necessary, a gaseous mixture containing propylene and 0.05% 1-^{13}C-ethylene.

The polymerization was stopped with 50 mL of 1-propanol acidified with HCl. The collected polymer (1.05 g), washed with methanol and dried in vacuum, was extracted with boiling *n*-heptane, and the *n*-heptane-insoluble fraction (98% of the whole polymer) was examined.

Table I
^{13}C Chemical Shifts Observed in TMU and in the Ethylene-Propylene Copolymer

	meso form	racemic form
(a) TMU; C-C-C-C-C-C-C-C-C-C-C (1 2 3 4 5 6 7 8 9 10 11)		
$C_{4'}$–$C_{8'}$	18.3_2	18.2_8
C_1–C_{11}	20.8_0	20.8_0
$C_{2'}$–$C_{10'}$	21.5_5	21.5_5
C_6	22.6_6	22.6_6
C_2–C_{10}	24.0_4	24.0_4
C_4–C_8	29.2_2	29.1_7
C_5–C_7	36.3_7	36.4_1
C_3–C_9	45.6_3	45.5_9
(b) Ethylene–Propylene Copolymer		
CH_3 [c]	19.7_9	
C_6	22.5_0	
CH[c]	27.0_0	
C_5–C_7	35.9_2	
CH_2 [c]	44.5_9	

[a] Chemical shifts are in parts per million downfield from HMDS. [b] According to a previous paper,[12] C_1 and C_{11} are considered the methyl carbons of isopropyl groups in the threo steric relationship with $C_{4'}$ and $C_{8'}$, respectively. $C_{2'}$ and $C_{10'}$ are considered those in the erythro relationship. [c] CH_3, CH_2, and CH are the inner methyl, methylene, and methine carbons of isotactic polypropylene blocks.

Both TMU and the ethylene–propylene copolymer were examined in 1,2,4-trichlorobenzene solution (20% by weight) using HMDS (1%) as an internal standard.

Samples were placed in 10 mm o.d. tubes containing a coaxial capillary of Me_2SO-d_6 for field-frequency stabilization. Spectra were measured with an HX-90 Bruker spectrometer operating at 22.63 MHz in the PFT mode. The temperature of the probe was 140 °C, and the variable temperature unit was checked with the ethylene glycol sample before the runs. Dwell time of 184 μs was used with 16K of computer memory for the interferogram, corresponding to an acquisition time of 3 s and to a digital resolution of 0.015 ppm/address. The pulse width was 3.5 μs (the pulse width for a 90° pulse for the nucleus being examined is 15 μs). No exponential weighting function of the FID was used.

All the chemical shifts observed are reported in Table I.

The assignment of the chemical shifts follows ref 7–12. For the assignment of the diastereomeric carbons of TMU (see the table), the relative intensity[2] of the peaks was also considered because the racemic form was more abundant than the meso form in view of the synthesis from partially resolved reagents.

Acknowledgment. Thanks are due to Mr. G. Zannoni for technical assistance in performing the NMR spectra.

References and Notes

(1) A. E. Tonelli, *Macromolecules*, **11**, 634 (1978).
(2) A. Zambelli, G. Bajo, and E. Rigamonti, *Makromol. Chem.*, **179**, 1249 (1978). This paper was not available to Dr. Tonelli when ref 1 was written.
(3) G. Natta, I. Pasquon, A. Zambelli, and G. Gatti, *J. Polym. Sci., Part A-1*, 403 (1963).
(4) A. Zambelli, G. Gatti, M. C. Sacchi, W. O. Crain, Jr., and J. D. Roberts, *Macromolecules*, **4**, 475 (1971).
(5) J. M. Sanders and R. A. Komoroski, *Macromolecules*, **10**, 1214 (1977).
(6) Unpublished data from our laboratory.
(7) D. M. Grant and E. G. Paul, *J. Am. Chem. Soc.*, **86**, 2984 (1964).
(8) L. F. Johnson, F. Heatley, and F. A. Bovey, *Macromolecules*, **3**, 175 (1970).
(9) W. O. Crain, Jr., A. Zambelli, and J. D. Roberts, *Macromolecules*, **4**, 330 (1971).
(10) A. Zambelli and G. Gatti, *Macromolecules*, **11**, 465 (1978).
(11) C. J. Carman, A. R. Tarpley, Jr., and J. H. Goldstein, *Macromolecules*, **6**, 719 (1973).
(12) A. Zambelli, P. Locatelli, and G. Bajo, *Macromolecules*, **12**, 154 (1979).