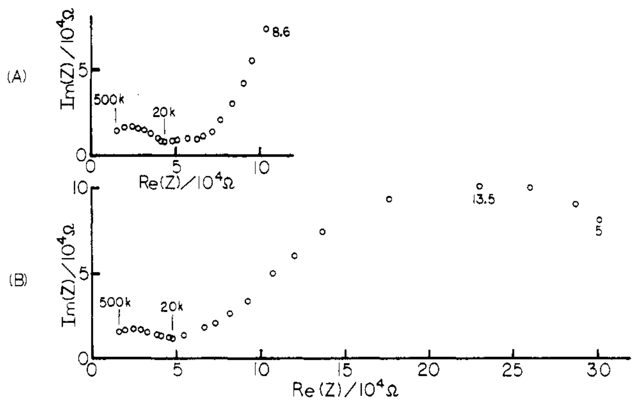

Figure 3. Plots of the imaginary part vs. the real part of the impedance (Z) for the 2:1 chloride: hydroxyl electrolyte at 60 °C. Frequencies (5 Hz to 500 kHz) are listed next to the data points. (A) With Pt electrodes; (B) with Hg/Hg_2Cl_2, calomel, electrodes.

To provide a definitive assignment of the low-frequency spur, calomel electrodes were employed in a second set of complex impedance expts. The spur seen previously for ion-blocking electrodes is now converted to an arc, Figure 3B. According to impedance/frequency response theory,[18] this arc can be ascribed to charge-transfer resistance at the chloride ion reversible electrode. This type of response is well characterized for other polymer electrolyte systems with cation reversible electrodes.[5,6]

The present work demonstrates that conductivity due to anion transport in a solvent-free polymer system can be on the same order of magnitude as that found for poly(ethylene oxide)–alkali metal salt systems. The electrical properties characterized in the present system may be attributed solely to the anion since the positive countercharge is anchored in the polymer backbone.

Acknowledgment. This research was partially supported by a grant from the Office of Naval Research. L.C.H. was the recipient of a DOE summer research fellowship administered by the Electrochemical Society. We appreciate helpful discussions with M. A. Ratner.

Registry No. Poly(diallyldimethylammonium chloride), 26062-79-3; poly(ethylene glycol), 25322-68-3; chloride, 16887-00-6.

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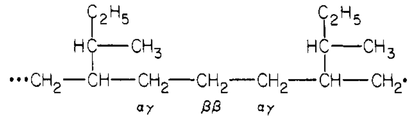
Leslie C. Hardy and Duward F. Shriver*
Department of Chemistry and Materials Research Center
Northwestern University, Evanston, Illinois 60201

Received November 29, 1983

Ethylene Units in $Al(CH_3)_3$-Cocatalyzed Polymerization of 3-Methyl-1-pentene

As reported in a previous paper,[1] ^{13}C-enriched C_2H_4 comonomer units have been detected in poly(3-methyl-1-pentene) prepared in the presence of the catalytic system δ-$TiCl_3/Al(^{13}CH_3)_3/Zn(^{13}CH_3)_2$



Two weak resonances of similar intensity have been detected in the ^{13}C NMR spectrum of this polymer (Figure 1) at 21.5_5 and 27.6_0 ppm for $\beta\beta^{2,3}$ and $\alpha\gamma$ (enriched) methylene carbons. The reason for the similar intensity of the $\beta\beta$ and $\alpha\gamma$ resonances in Figure 1 is that the $\alpha\gamma$ resonance from 3-methyl-1-pentene units is so low as to go undetected. In principle, a small amount of 1-^{13}C-enriched C_2H_4 could appear in the system and copolymerize as a consequence of metathesis involving ^{13}C-enriched metallocarbenes and 3-methyl-1-pentene.

$$\begin{array}{c} Mt{=}^{13}CH_2 + CH_2{=}CH{-}CH(CH_3)C_2H_5 \\ \uparrow\downarrow \\ Mt{=}CH{-}CH(CH_3)C_2H_5 + CH_2{=}^{13}CH_2 \end{array} \quad (1)$$

It may be worthwile to mention that metallocarbenes have been suggested to play a role even in olefin insertion.[4] On the other hand, one could conjecture that 1,2-^{13}C-enriched C_2H_4 results from decomposition of two $Mt{-}^{13}CH_3$ bonds through a more or less complicated reaction pathway,[5] e.g.

$$2Mt{-}^{13}CH_3 \rightarrow {}^{13}CH_2{=}^{13}CH_2 + \text{decomposition products} \quad (2)$$

In principle, one could discriminate between the presence of either 1-^{13}C-enriched ethylene or 1,2-^{13}C-enriched ethylene by observing the $^{13}C{-}^{13}C$ satellites. However, the relatively low enrichment (30%) of the $Al(CH_3)_3$ and $Zn(CH_3)_2$ used,[1] as well as the low content of C_2H_4 in the polymer, precludes such a possibility. On the other hand, when 1-^{13}C-enriched 3-methyl-1-pentene is polymerized in the presence of δ-$TiCl_3/Al(CH_3)_3/Zn(CH_3)_2$, 1-$^{13}C$-enriched C_2H_4 is still expected by metathesis, while unenriched ethylene is expected from the decomposition reaction.

The spectrum of poly-(3-methyl-1-pentene-*1*-^{13}C) prepared with δ-$TiCl_3/Al(CH_3)_3$ is reported in Figure 2. It may be observed that the resonance at 27.5_7 ppm ($\alpha\gamma$-methylene carbons) is still present while that at 21.5_5 ppm has disappeared. This is just what one would expect from the presence of unenriched ethylene units. As a matter of fact, the $\alpha\gamma$-enriched methylene carbons can arise either

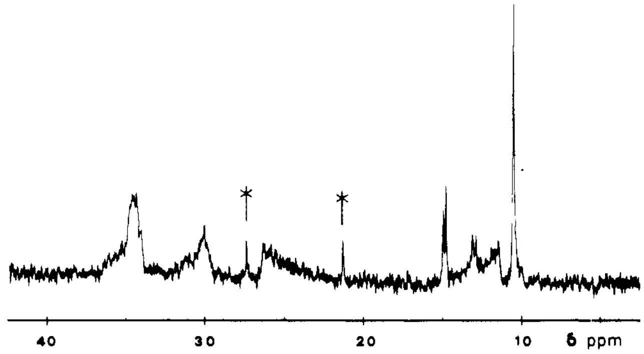


Figure 1. ^{13}C NMR spectrum of the benzene-soluble fraction of isotactic poly[(*RS*)-3-methyl-1-pentene]. The resonances marked by asterisks are due to ^{13}C-enriched $\beta\beta$ (21.5_5 ppm) and $\alpha\gamma$ (27.6_0) methylene carbons (HMDS scale).

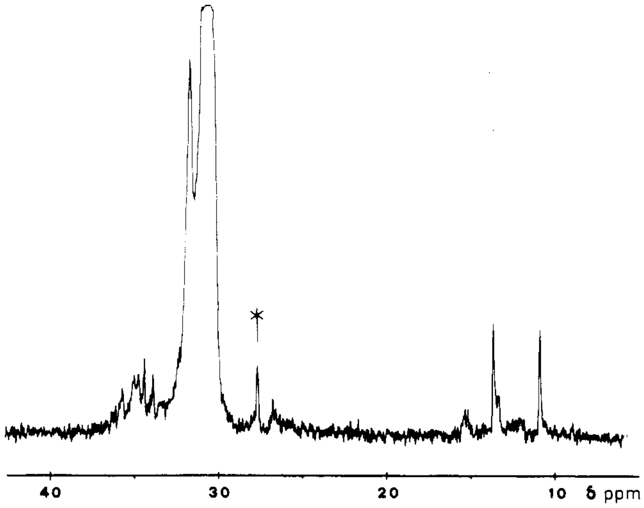


Figure 2. ^{13}C NMR spectrum of the benzene-soluble fraction of poly[(*RS*)-3-methyl-1-pentene-*1*-^{13}C]. The resonance marked by an asterisk is due to ^{13}C-enriched $\alpha\gamma$-methylene carbons (HMDS scale).

from enriched ethylene or from 1-^{13}C-enriched 3-methyl-1-pentene, while $\beta\beta$-enriched carbons can only come from enriched ethylene.

It can be concluded that ethylene incorporation occurs via a decomposition route. The absence of metathesis is some not irrelevant evidence for the mechanism of insertion of α-olefins in Ziegler–Natta polymerization.[6]

Experimental Section. The synthesis of (*RS*)-3-methyl-1-pentene-*1*-^{13}*C*) and of Al(^{13}CH$_3$)$_3$, together with the polymerization and fractionation conditions, were described in ref 1.

^{13}C NMR analysis of the polymers dissolved in 1,2,4-trichlorobenzene containing 1% HMDS as an internal standard was carried out at 140 °C in the PFT mode on a Bruker HX-90 spectrometer operating at 22.63 MHz. Pulse width: 3.6 μs.

Acknowledgment. Financial support by the Italian "Programma Finalizzato di Chimica fine e Secondaria" is gratefully acknowledged.

Registry No. Al(CH$_3$)$_3$, 75-24-1; Zn(CH$_3$)$_2$, 544-97-8; poly[(*RS*)-3-methyl-1-pentene) (homopolymer), 66906-10-3; ethylene, 74-85-1; isotactic poly[(*RS*-3-methyl-1-pentene] (homopolymer), 88611-18-1.

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(2) The assignment has been confirmed by observing the ^{13}C NMR spectrum of a copolymer obtained by adding ethylene-*1*-^{13}*C* in the feed. The backbone methylene carbons are labeled according to the distance from the tertiary carbons. Carman, C. J.; Wilkes, C. E. *Rubber Chem. Technol.* **1971**, *44*, 481.

(3) Two resonances should be expected for the $\alpha\gamma$-methylene carbons in view of the stereochemical effect on the chemical shift of the substituent of the neighboring 3-methyl-1-pentene unit. Most probably, one of them is overlapped with the other resonances.

(4) The metallocarbene species could be formed, for example, by hydrogen migration from the α carbon to the metal. Ivin, K. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L. H.; Mathab, R. *J. Chem. Soc., Chem. Commun.* **1978**, 604.

(5) Another possibility could be

$$\mathrm{Mt}\text{-}(^{13}\mathrm{CH}_3)_2 \rightarrow {}^{13}\mathrm{CH}_2{=}{}^{13}\mathrm{CH}_2 + \text{decomposition products}$$

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

Adolfo Zambelli* and Paolo Ammendola
Istituto Chimico, Università di Napoli
80134 Napoli, Italy

Paolo Locatelli and Maria Carmela Sacchi
Istituto di Chimica delle Macromolecole del CNR
20132 Milano, Italy

Received October 19, 1983

Proton Resonance Assignments in Copolymer Spectra by Two-Dimensional NMR

Nuclear magnetic resonance (NMR) spectroscopy is a powerful tool for the analysis of the microstructure of copolymers since the comonomer sequences can be directly observed. If the resonance lines can be assigned to specific sequences, the line intensities can be used to characterize the kinetics of the copolymerization process. We report a novel application of two-dimensional nuclear Overhauser effect (2D NOE) spectroscopy to the assignment of tetrad sequence resonances in the proton spectrum of a copolymer.

2D NOE spectroscopy is only one of a number of two-dimensional NMR experiments that are all based on the same general principles. Two-dimensional NMR was first conceived by Jeener in 1971[1] but his ideas were not widely appreciated until Ernst et al. performed the first experiment in 1976.[2] Performed the first experiment in 1976.[2] 2D NMR spectroscopy can be divided into two broad categories: 2D resolved and 2D correlated. Two-dimensional resolved spectroscopy separates two different interactions along two frequency axes. An example is homonuclear 2D *J*-resolved spectroscopy, which displays the chemical shift along one axis and the *J* coupling along the other. In 2D-correlated spectroscopy, chemical shifts are plotted along both axes but are correlated by a particular interaction between them. In 2D NOE spectroscopy, the correlating interaction is the nuclear Overhauser effect. The result of a 2D NOE experiment is a map of the entire network of nuclear Overhauser effects between protons in the molecule.

Two-dimensional NMR techniques have been applied extensively to biological molecules.[3] In particular, 2D NOE experiments have been performed by Wüthrich, Ernst, and others on proteins,[8–14] cyclic peptides,[15,16] micelle-bound glucagon,[17] nucleic acids,[18,19] and synthetic biopolymers.[20] Macura and Brown[21] have applied 2D *J*-resolved spectroscopy to poly(vinyl chloride), and Gerig[22] has applied ^{19}F–^{1}H 2D chemical shift correlated NMR to poly(*p*-fluorostyrene). However, there have been no applications of 2D NOE spectroscopy to synthetic polymers.

2D NOE Spectroscopy. The pulse sequence for 2D

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