possibly for PE also. It is beyond the scope of this present study to formulate models more consistent with the observations.

Finally, the conclusion that diffusion through PTFE proceeds at least in part along pores and grain boundaries may have a significance far beyond the diffusion process. Other observed properties of bulk PTFE, which have been ascribed to the dense polymer structure itself, may also be due in part to the physical structure of the sintered material. A re-evaluation of PTFE properties on the basis of this model may well be worthwhile.

Acknowledgment. M. Christensen assisted in the experimental work and F. J. Martinelli wrote the computer programs. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration under Contract No. NAS 7-698.

Nuclear Magnetic Resonance Spectroscopy. Steric Control in α-Olefin Polymerization as Determined by ^{13}C Spectra

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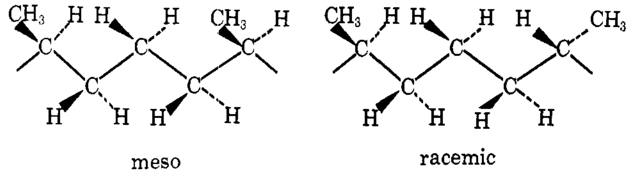
ABSTRACT: Carbon-13 nmr spectroscopy has been used to elucidate the stereochemistry of ethylene–propylene copolymers prepared from enriched ethylene-*1*-^{13}*C*. The results give useful information on the degree and source of steric control in isospecific and syndiospecific polymerizations of α olefins.

The ^{13}C (cmr) spectra of ethylene–propylene copolymers prepared in the presence of isospecific catalysts appear to show only two resonance peaks for a single ethylene unit flanked by propylene units.[2] The lower field absorption has been ascribed to the lateral CH$_2$ and the higher field absorption to the central CH$_2$ of the (CH$_2$)$_3$ sequences. *A priori*, such (CH$_2$)$_3$ sequences could lie in a meso (m) configuration or in a racemic (r) configuration, depending on the relative stereochemical arrangements of the contiguous propylene units. Thus, if there are only two ethylene resonances for the (CH$_2$)$_3$ sequences, this suggests that for these copolymers only the meso (or only the racemic) situation occurs. Actually, occurrence of only racemic sequences seems quite improbable because of the isospecific nature of the polymerizations. However, it might also be possible that both meso and racemic situations occur, but that the carbon chemical shifts are insensitive to the configurations. We have now clarified this point and reached some conclusions on the mechanism of steric control in α-olefin polymerization by comparing the cmr spectra of copolymers made with ^{13}C-enriched ethylene and isospecific catalysts with those of similar copolymers prepared in the presence of syndiospecific and aspecific catalysts.



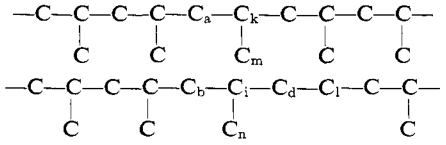
meso racemic

Results and Discussion

Figures 1a and 1b show the cmr spectra of two samples of 1-^{13}C 60%-enriched ethylene with ordinary propylene. Sample A contains 9 mol % ^{13}C-enriched ethylene and was prepared by the syndiospecific catalyst VCl$_4$–Al(C$_2$H$_5$)$_2$Cl. Sample B contains 9 mol % ^{13}C-enriched ethylene and was prepared by the aspecific catalyst VCl$_4$–Al(C$_2$H$_5$)$_3$. X-Ray and infrared analyses of these samples show that the steric arrangement in propylene blocks is syndiotactic in sample A and atactic in sample B as in the corresponding homopolymers. Therefore, the copolymerization with ethylene does not change the basic stereospecific behavior of the catalysts. In addition, the infrared analysis suggests the presence of –CH(CH$_3$)(CH$_2$)$_2$CH(CH$_3$)– sequences to the extent of 8% (g of CH$_2$/100 g of copolymer) in sample A and 4% in sample B.

The product of the reactivity ratios for both catalyst systems is equal to or less than unity[3] and this fact, along with the low incorporation of C$_2$H$_4$, requires that the greater part of the ethylene units be isolated between propylene units. Comparison of similar nonenriched copolymers permits the assignments, without uncertainty, of the starred peaks of Figures 1a and 1b to carbons in the chain arising from ethylene.

Table I contains the chemical shifts of the resonances detected in samples A and B and in a similar sample (C) prepared in the presence of an isospecific catalyst. The carbons are labeled as in the previous paper, where a partial assignment of the chemical shifts was made.[2b] In addition,



$$\begin{array}{cccccccccccc}
— & C— & C— & C— & C— & C_a— & C_k— & C— & C— & C— & C— \\
 & | & & | & & & | & & | & & | \\
 & C & & C & & & C_m & & C & & C \\
— & C— & C— & C— & C— & C_b— & C_i— & C_d— & C_l— & C— & C— \\
 & & | & & | & & | & & & & | \\
 & & C & & C & & C_n & & & & C
\end{array}$$

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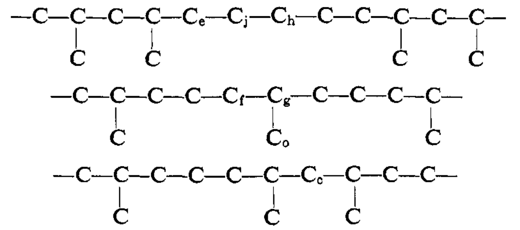
[1] (a) Contribution No. 4236. (b) That part of this research carried on at the California Institute of Technology was supported by the National Science Foundation.

[2] (a) A. Zambelli, "NMR Basic Principles and Progress," Vol. 4, Springer-Verlag, Heidelberg, 1971, p 101. (b) W. O. Crain, Jr., A. Zambelli, and J. D. Roberts, *Macromolecules*, **4**, 330 (1971).

[3] A. Zambelli, A. Léty, C. Tosi, and I. Pasquon, *Makromol. Chem.*, **115**, 73 (1968).

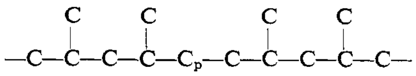


$$-C-\underset{\substack{|\\ C}}{C}-C-\underset{\substack{|\\ C}}{C}-C_e-C_j-C_h-C-C-\underset{\substack{|\\ C}}{C}-C-\underset{\substack{|\\ C}}{C}-$$

$$-C-\underset{\substack{|\\ C}}{C}-C-C-C_f-\underset{\substack{|\\ C_o}}{C_g}-C-C-C-\underset{\substack{|\\ C}}{C}-$$

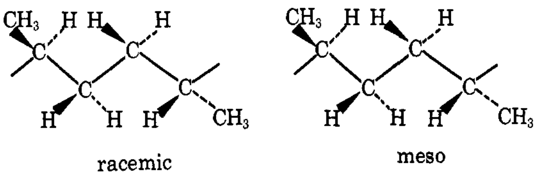
$$-C-\underset{\substack{|\\ C}}{C}-C-C-C-\underset{\substack{|\\ C}}{C}-C_c-\underset{\substack{|\\ C}}{C}-C-C-$$

because of the presence of $(CH_2)_2$ in samples A and B, the following arrangement was also considered.



$$-C-\overset{\substack{C\\ |}}{C}-C-\overset{\substack{C\\ |}}{C}-C_p-C-\overset{\substack{C\\ |}}{C}-C-\overset{\substack{C\\ |}}{C}-C-$$

The p carbons, like the d and l carbons, can lie between a pair of racemic or meso propylene units. Table I also shows



racemic meso

calculated chemical shifts according to Grant and Paul,[4] which, however, do not take stereoisomerism into account. Considering the isolated ethylene d, l, and p carbons in samples A and B, we expect a minimum of six peaks, namely d(m), d(r), l(m), l(r), p(m), and p(r), where the intensities of the peaks will be such that [d(m)] = [l(m)] and [d(r)] = [l(r)]. Actually, there are five observed ethylene carbon resonances for these samples.

Disregarding possible perturbations from unequal Overhauser effects, we can account for the results by saying that all the possible ethylene carbons, d(m), d(r), l(m), l(r), p(m), and p(r), are present in the A and B copolymers, and that the chemical shifts of the l(m) and l(r) carbons accidentally coincide.

There are only two peaks of equal intensity for the isospecific copolymer (sample C),[2a] which indicates the presence of only d(m) and l(m) carbons because the d(r) peak, if present, should be easily distinguishable from the d(m) carbon peak as for samples A and B.

The peaks of the p carbons can be distinguished from those of the d carbons by considerations of peak intensities. In addition, the p-carbon chemical shifts agree with the calculated values. To confirm these conclusions, especially in regard to (1) the chemical shift of the l carbon and (2) the sensitivity of the p-carbon shift to the stereochemical arrangement, we have examined the cmr spectra of 3,7-dimethylnonane and of two samples of nearly alternating *cis*-2-butene–ethylene and *trans*-2-butene–ethylene copolymers (Figure 2).

TABLE I
CHEMICAL SHIFTS OF PROPYLENE–ETHYLENE COPOLYMERS[a]

Carbon	A (syndiotactic)	B (atactic)	C (isotactic)	Calcd
CH_3	18.0	18.0	*b*	
	18.6	18.7		
	19.5	19.6		
CH_2 l	22.9	23.1	23.1	23.7
CH k	26.1	26.1		25.5
CH i	29.3	29.2		
CH_2 p	32.8	32.9		33.5
	33.7	34.1		
CH_2 d	35.8	36.1	36.2	36.2
	36.8	37.0		
CH_2 a	44.6	44.7		43.1

[a] All chemical shifts are in parts per million downfield from HMDS. [b] Not determined.

TABLE II
CHEMICAL SHIFTS OF THE 2-BUTENE–ETHYLENE COPOLYMERS[a]

	Exptl		
Carbon	Cis	Trans	Calcd
CH_3	14.8	12.73	16.1
$(CH_2)_{n \geqslant 4}$	28.3[b]		
$(CH_2)_2$	29.5	28.5	30.9
CH[c]	36.6	35.5	38.2

[a] All chemical shifts are in parts per million downfield from HMDS. [b] This signal is assigned to sequences with $n \geqslant 4$ because the copolymer contains >50 mol % ethylene; the calculated shifts of the central CH_2 are 27.1 ppm for $n = 4$, 29.4 ppm for $n = 6$, and 28.7 ppm for $n = \infty$. [c] Note that also the methine chemical shift (unlike in polypropylene) is dependent on the steric arrangement.

The first copolymer is a crystalline material with p(m) carbons.[5] Its cmr spectrum shows four main peaks (Figure 2a), while the cmr spectrum of the *trans*-2-butene–ethylene copolymer shows three main peaks (Figure 2b). Comparison of the two spectra in the CH_2 region permits the conclusion that, for these copolymers, the chemical shift of the p carbon is sensitive to the steric arrangement of the tertiary carbons. The assignments in Table II were made with the aid of the Grant and Paul[4] correlation.

The chemical shift of the carbons of the 3,7-dimethyl-

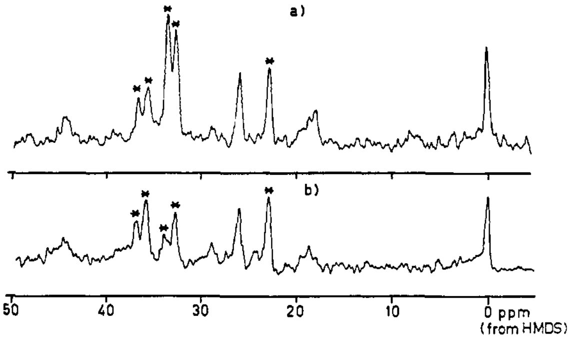


Figure 1. Cmr spectra of ethylene–propylene copolymers made with enriched ethylene-*1*-^{13}C: (a) sample A and (b) sample B.

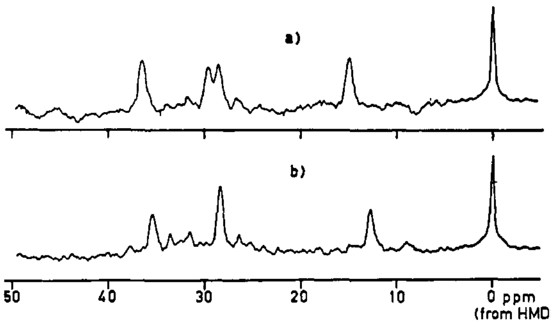


Figure 2. Cmr spectra of nearly alternating copolymers of (a) *cis*-2-butene–ethylene and (b) *trans*-2-butene–ethylene.

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(4) D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, **86**, 2984 (1964).

(5) G. Natta, P. Corradini, P. Ganis, I. W. Bassi, and G. Allegra, *Chim. Ind. (Milan)*, **44**, 532 (1962).

TABLE III
CHEMICAL SHIFTS OF 3,7-DIMETHYLNONANE[a]

Carbon	Exptl	Calcd
1	9.5	9.8
(3-CH_3)	17.5	18.0
5	23.3	23.5
2	28.0	28.2
3	33.0	32.6
4	35.5	35.1

[a] All chemical shifts are in parts per million downfield from HMDS.

nonane (Table III) have been assigned by off-resonance decoupling and peak intensities. They agree well with the predictions of the Grant and Paul procedure.

However, it must be noted that resonances of racemic and meso 3,7-dimethylnonane cannot be distinguished at 22.6 MHz and are, at best, marginally different at 55 MHz.[6] Apparently, the differences induced by CH_3 and C_2H_5 substituents are not sufficiently large to be easily detectable, although this is not what is expected on the basis of previous work on related substances.[7]

We believe that the following conclusions can be drawn from the results. (1) In the ethylene–propylene copolymers obtained with isospecific catalysts, the ethylene units appear to occur only in meso-type situations. This, taken in conjunction with the fact that the polymerization occurs by insertion in a metal–carbon bond,[8–10] indicates that the mechanism of isotactic stereoregulation is not an asymmetric induction involving only the last unit of the growing chain end. Stereoregulation occurs when the last unit is unsubstituted, and, because a terminal ethylene unit should be able to rotate freely, it seems likely that dissymmetry around the metal atom provides control of the stereochemistry of the addition. (2) Because in the syndiotactic ethylene–propylene copolymers ethylene appears to occur with comparable frequency between meso-like and racemic-like propylene units, it seems reasonable that steric control with syndiospecific catalysts is exerted by the last unit of the growing chain end. (3) Comparison of the chemical shifts of the d carbons in samples A, B, and C (remembering that only d(m) carbons are expected in sample C) permits identification of the d(m) carbons at 35.8, 36.1, and 36.2 ppm, respectively, and d(r) at 36.8 and 37.0 ppm, respectively. In the A and B samples, d(m) carbons predominate over d(r) carbons. This can be explained by assuming that, on insertion of an ethylene unit, the penultimate (propylene) unit has a low potential for asymmetric induction which is opposite to that usually exerted by the last unit. Alternatively, and perhaps more reasonably, the transition metal atom in the catalyst is dissymmetric, not only for the isospecific catalyst complexes but for the syndiospecific and aspecific ones as well. With the isospecific catalysts, the steric bulkiness of the catalyst may be large enough to lead to predominate asymmetric induction by the catalyst. With the syndiospecific catalysts, asymmetric induction by the last monomer unit could be greater than that of the catalyst, while in the aspecific polymerization, the two inducing influences could be opposite and essentially equal.

Experimental Section

Polymerizations. The A and B samples were prepared at −78° with low conversion of both monomers by VCl_4–$Al(C_2H_5)_2Cl$ (syndiospecific) and VCl_4–$Al(C_2H_5)_3$ (aspecific) catalyst systems in *n*-heptane.[8,11] The C sample was prepared at 15° by $TiCl_3$–$Al(C_2H_5)_2I$ catalst sysytem in *n*-heptane.[12] The raw polymer was extracted with boiling *n*-heptane; the C sample was the *n*-heptane insoluble fraction. The constancy of the monomer concentrations was ensured by monitoring the partial pressures and introducing, as necessary, a mixture of the monomers of proper composition. The raw 2-butene–ethylene copolymers were prepared as previously described.[13] The boiling *n*-hexane soluble, boiling *n*-pentane insoluble fraction of *cis*-2-butene–ethylene copolymer and the boiling *n*-pentane soluble fraction of *trans*-2-butene–ethylene copolymer are the samples whose spectra are shown in Figure 2.

Characterization of the Copolymers. The presence of $(CH_2)_2$ sequences in the A and B samples was indicated by infrared analysis according to Bucci and Simonazzi.[14] The syndiotactic arrangement of the propylene unit blocks in sample A was confirmed by the infrared absorption at 11.5 μ.[8] Sample C showed an X-ray spectrum quite similar to that of isotactic polypropylene.[15] The per cent of ethylene in the copolymers was detected by radiochemical analysis of the samples prepared under the same conditions as samples A, B, and C, by using ^{14}C-labeled ethylene. The infrared analysis gives the total $(CH_2)_2$, whereas the cmr analysis of samples A and B gives the $(CH_2)_2$ derived from ethylene units.

The cmr spectra were recorded with a Bruker HFX-90 spectrometer at 22.62 MHz with wide-band proton decoupling, and were accumulated with a Fabritek 1074 computer. The oscillator frequency was obtained from a Schromandl ND100 M frequency synthesizer locked to the master oscillator in order to avoid drifts during the accumulation.

The solvent was *o*-dichlorobenzene, the reference was the peak of hexamethyldisiloxane (HMDS), and the nmr stabilization was obtained through heteronuclear lock to the ^{19}F signal of hexafluorobenzene.

Samples were completely dissolved by heating and then observed at the probe temperature which was about 50°, owing to the radiofrequency power required for proton decoupling.

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(6) Kindly determined by Dr. C. Marzin with the 55-MHz Varian superconducting cmr spectrometer.

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