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^{13}C NMR Studies of Ethylene–Propylene Copolymers Prepared with Homogeneous Metallocene-Based Ziegler–Natta Catalysts

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ABSTRACT: The recent discovery of homogeneous metallocene-based Ziegler–Natta catalysts has led to the synthesis of EP copolymers with new comonomer and stereochemical structures. In the present paper ^{13}C NMR investigation of EP copolymers at high ethylene content, prepared with highly isospecific, highly syndiospecific, and aspecific catalysts, is presented. The high stereoregularity of the iso- and syndiotactic samples and the complete regioregularity of all three samples greatly simplify the spectra and make it possible to check some of the chemical shift predictions and to perform other sequence assignments. The assignment of new sequences is based on (i) correlation of chemical shifts of homo- and copolymers performed with the same catalysts, (ii) comparison of spectral intensities for samples of different compositions, and (iii) comparison with chemical shift values predicted by calculations. The detailed information obtained on comonomer and tactic sequences opens the possibility of describing the chain growth mechanism for the various catalytic systems and of correlating chain structure and copolymer physical and mechanical properties.

Introduction

Ethylene–propylene copolymers are industrially important materials. Since their physical and mechanical properties depend on their structures, over the years several ^{13}C NMR studies have been performed for their characterization.

Starting from the fundamental work by Carman and Wilkes,[1] a comprehensive analysis of ethylene–propylene copolymers, mainly made with aspecific vanadium-based Ziegler–Natta catalysts, has been performed.[2–4] These copolymers contain both isotactic and syndiotactic propene sequences, and head to head and tail to tail structures accompany the normal head to tail insertion of propene. The sum of contributions of ethylene–propylene sequence placement, propylene tacticity, and propylene inversion makes the features of the ^{13}C NMR spectra of these copolymers very complex, and though many tactic, propene inversion, and comonomer sequence dependent resonances have been assigned, a complete description of the copolymers only by comonomer triads is possible so far.

Ethylene–propylene copolymers made with isospecific heterogeneous Ziegler–Natta catalysts have been widely studied also.[5–7] The simplification due to the high stereospecificity of these catalysts and to the absence of propene inversion led to the assignment of longer sequences than in the copolymer made with the vanadium-based catalysts. Recently, by using the ^{13}C NMR γ effect, Mark's rotational isomeric model, and the 2D-INADEQUATE NMR technique, Hayashi et al. have obtained a complete pentad assignment of methyl and methine-centered resonances in EP copolymers at low ethylene content, made with the $TiCl_3/AlEt_2Cl$ catalytic system.[8] Calculations still based on the γ effect and Mark's rotational isomeric model have also allowed the same authors to predict the chemical shifts of methylene carbon dependent on the hexad comonomer sequences in many of the possible stereosequences.[9,10] Such predictions were verified on an isotactic copolymer at low ethylene content and in a prevailingly atactic fraction of the same copolymer.

The recent discovery of homogeneous metallocene-based Ziegler–Natta catalysts has opened the possibility of synthesizing EP copolymers with new comonomer and stereochemical structures. This discovery leads to a novel interest in ^{13}C NMR investigation of EP copolymers since new materials have to be characterized. Moreover these new copolymers give the chance of checking some of the chemical shift predictions and of performing other sequence assignments.

In the present paper ^{13}C NMR investigation of EP copolymers at high ethylene content, prepared with highly isospecific, highly syndiospecific, and aspecific catalysts, is presented. The high stereoregularity of the iso- and syndiotactic samples and the complete regioregularity of all three samples greatly simplify the spectra. A comparison with the previously assigned and predicted chemical shifts is performed. The assignment of new sequences is based on (i) correlation of chemical shifts, using the results of highly resolved spectra of homopolymers prepared with the same catalysts; (ii) comparison of spectral intensities for samples of different compositions; and (iii) comparison with predicted chemical shift values obtained by Cheng's CALMOD computer program.[11]

The assignments of primary, secondary $S_{\alpha\alpha}$,[12] and tertiary carbons will be reported. These spectral regions that regard propene-centered sequences are better resolved than the regions that regard ethylene-centered sequences ($S_{\alpha\gamma}$, $S_{\alpha\delta}$, $S_{\beta\beta}$, $S_{\beta\delta}$, $S_{\gamma\gamma}$, $S_{\gamma\delta}$, $S_{\delta\delta}$).[12] The assignment and, in many cases, the quantitative evaluation of sequences as long as heptads and hexads are possible. On the basis of information as detailed as possible on comonomer and tactic sequences, the description of the chain growth mechanism for the various catalytic systems and the correlation between chain structure and copolymer physical and mechanical properties could be obtained.

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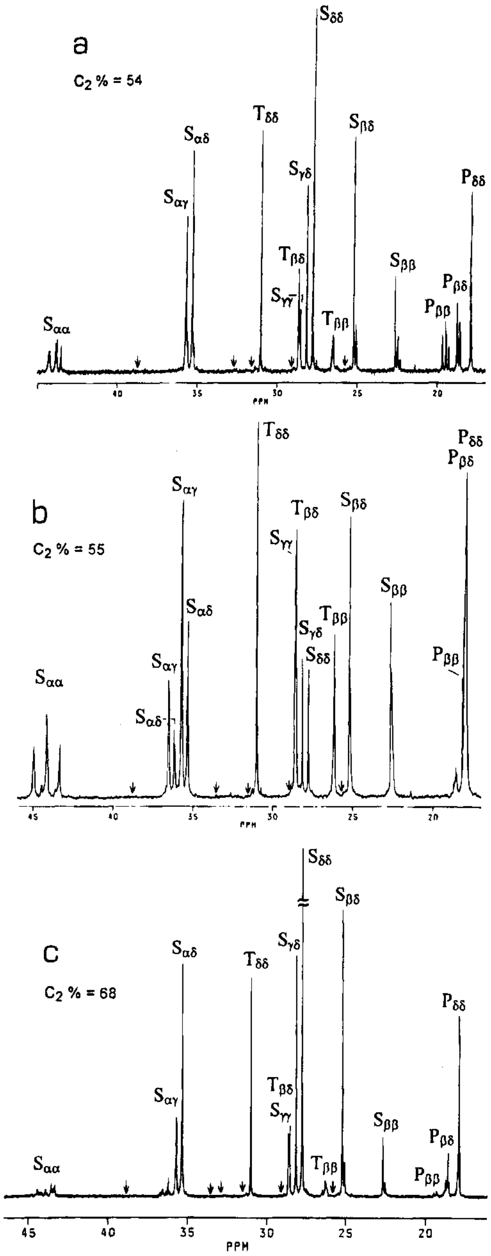


Figure 1. ^{13}C NMR spectra of ethylene−propylene copolymers prepared with isospecific (a), syndiospecific (b), and aspecific (c) catalysts.

Results and Discussion

In Figure 1 the spectra of EP copolymers, prepared with highly isospecific, highly syndiospecific, and completely aspecific catalysts are shown. The spectrum terminology follows that of Carman and Wilkes, where S, T, and P refer respectively to the secondary (methylene), tertiary (methine), and primary (methyl) carbons. The two Greek subscripts indicate the distances of the carbon in question from the neighboring methines.

The copolymers are completely regiospecific. Indeed, the resonances of the sequences arising from the meso and racemic inverted propene are absent. (See Chart 1.) The arrows in the spectra show the open regions in which the resonances assigned to these structures should appear.

Methyl Region. Figure 2 shows the expanded plot of the methyl region of the same copolymers. In the copolymer prepared with the isospecific catalyst (Figure 2a) the propene propagation is completely stereospecific. The arrows in the spectrum show the chemical shifts corresponding to the pentad containing the most common isolated steric errors:

$$P^mP^m\underline{P}^rP^rP = 18.90 \text{ ppm}$$

$$P^mP^r\underline{P}^rP^mP = 17.68 \text{ ppm}$$

where P^mP and P^rP represent the isotactic and syndiotactic propene diads, respectively. The central propene of the sequences, whose methyl signal is observed, is underlined. Similarly, in the following, the central propene diad of the sequences, whose methylene signal is observed, and the central propene of the sequences, whose methine signal is observed, are underlined.

Due to the absence of stereoirregularities the spectral multiplicity can be ascribed to differences in EP sequences only. In Table 1 the observed chemical shifts and assignments for primary carbons are given. The chemical shift differences are compared with those given in the literature.[8] There is close agreement between the two sets of assignments.

The resonances of the methyl region can be easily explained in terms of mainly additive effects arising from substitution of P with E at different distances from the observed carbon. If the signal of the isotactic heptad is taken as the reference chemical shift, the substitution of P with E always gives a higher field shift of the central methyl observed, in agreement with the empirical additivity rules.[13] However the effects are not wholly additive, as the introduction of E on one side decreases the effect of the same substitution on the other side.

In fact, taking the signal of the isotactic pentad $P^mP^m\underline{P}^mP^mP$ as the reference chemical shift (19.68 ppm as the average of resonances 1 and 2), we observe that (i) the substitution of the P adjacent to the central $\underline{P}$ on one side ($P^mP^m\underline{P}EP$, 18.76 ppm as the average of resonances 6 and 7) gives an upfield shift of 0.92 ppm, while the substitution of the P in the same position on the other side ($PE\underline{P}EP$, 17.93 ppm) gives an upfield shift of 0.83 ppm; and (ii) the substitution of the P's next to the adjacent P's ($P^mP^m\underline{P}^mPE$, 19.46 ppm as the average of resonances 3 and 4; $EP^m\underline{P}^mPE$, 19.28 ppm, resonance 5) gives upfield shifts of 0.22 and 0.18 ppm, respectively.

When the signal of the isotactic heptad $P^mP^mP^m\underline{P}^mP^mP^mP$ is taken as the reference chemical shift (19.70 ppm, resonance 1), the substitution of a further P ($P^mP^mP^m\underline{P}^mP^mPE$, 19.66 ppm, resonance 2) gives a smaller upfield shift of 0.04 ppm on one side (the same chemical shift difference is observed between resonances 6 and 7), while the corresponding substitution on the other side gives even less or no detectable chemical shift variation.

Moreover the introduction of E on one side decreases or cancels the effect of further substitution on the same side. After the substitution of the P's adjacent to the central propene, a further substitution gives an upfield shift of 0.02−0.04 ppm (see for instance the chemical shift differences between resonances 6 and 8 or between resonances 12 and 13). After the substitution of the P's next to the adjacent P's we cannot obtain any further information. As a consequence only the isotactic propene heptad is assigned and a complete quantitative evaluation only of the methyl-centered comonomer pentads can be obtained.

Figure 2b shows the expanded plot of the methyl region of two copolymers of different composition prepared with the syndiospecific catalyst. In Table 2 the

Table 1. Assignments for the Methyl Region (Isospecific Catalyst)

carbon	sequence[a]	no.	shift (ppm)	$\Delta\delta^b$ (ppm) this work	$\Delta\delta^b$ (ppm) lit.[8]
$P_{\beta\beta}$	$P^mP^mP^m\underline{P}^mP^mP^mP$	1	19.70	0.00	0.00
	$\square P^mP^m\underline{P}^mP^mPE$	2	19.66	-0.04	-0.04
	$P^mP^mP^m\underline{P}^mPE\square$	3	19.47	-0.23	-0.24
	$EP^mP^m\underline{P}^mPE\square$	4	19.44	-0.26	-0.27
	$EP^m\underline{P}^mPE$	5	19.28	-0.42	-0.38
$P_{\beta\delta}$	$P^mP^mP^m\underline{P}EP\square$	6	18.78	0.00	0.00
	$EP^mP^m\underline{P}EP\square$	7	18.74	-0.04	-0.04
	$P^mP^mP^m\underline{P}EE\square$	8	18.74	-0.04	
	$EP^mP^m\underline{P}EE\square$	9	18.70	-0.08	-0.08
	$EP^m\underline{P}EP$	10	18.60	-0.18	-0.18
	$EP^m\underline{P}EE$	11	18.56	-0.22	-0.21
$P_{\delta\delta}$	$PE\underline{P}EP$	12	17.93	0.00	0.00
	$PE\underline{P}EE$	13	17.90	-0.03	-0.02
	$EE\underline{P}EE$	14	17.88	-0.05	-0.05

[a] $\square$ = E or P. [b] Chemical shift differences relative to the values of $P^mP^mP^m\underline{P}^mP^mP^mP$, $P^mP^mP^m\underline{P}EP\square$, and $PE\underline{P}EP$, respectively, which are set to be 0 ppm.

Table 2. Assignments for the Methyl Region (Syndiospecific Catalyst)

carbon	sequence[a]	no.	shift (ppm)	$\Delta\delta^b$ (ppm) obsd	$\Delta\delta^b$ (ppm) calcd[c] [11]
$P_{\beta\beta}$	$P^r\underline{P}^rP$	15	18.13	0.00	0.00
	$EP^m\underline{P}^rPE$	16	18.70	0.57	0.54
$P_{\beta\delta}$	$P^rP^r\underline{P}EP$	17	18.01	0.00	0.00
	$EP^r\underline{P}EP$	18	18.05	0.04	0.10
	$P^rP^r\underline{P}EE+EP^r\underline{P}EE$	19	17.96	-0.05	0.03
	$P^rP^m\underline{P}E\square$	20	18.49	0.48	0.51
	$EP^m\underline{P}EP$	10	18.59	0.63	0.69
	$EP^m\underline{P}EE$	11	18.56	0.60	0.64
$P_{\delta\delta}$	$PE\underline{P}EP$	12	17.92		
	$PE\underline{P}EE$	13	17.90		
	$EE\underline{P}EE$	14	17.87		

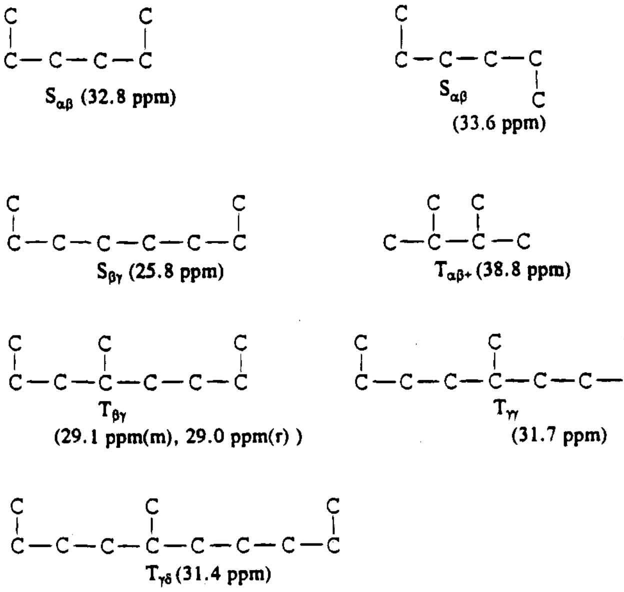
[a] $\square$ = E or P. [b] Chemical shift differences relative to the values of $P^v\underline{P}^rP$ and $P^rP^r\underline{P}EP$, respectively, which are set to be 0 ppm.

observed chemical shifts and assignments are given. The chemical shift differences, calculated by means of the CALMOD program, are given as well.

The syndiotactic pentad $P^rP^r\underline{P}^rP^rP$ has been assigned by comparison with the spectrum of the homopolymer obtained under the same conditions. According to the assignment given by Zambelli and Gatti on the model compound 2,4,6,8,10,14-hexamethylpentadecane,[14] the substitution of the last P of the pentad ($P^rP^r\underline{P}^rPE$) should give a downfield shift of the central methyl of 0.02 ppm. Actually, no peak occurs slightly downfield from the narrow signal at 18.13 ppm assigned to the syndiotactic pentad. Since the analysis of the methylene and methine regions of the spectrum ($S_{\alpha\alpha}$ and $T_{\beta\beta}$, see below) shows that a noticeable amount of syndiotactic propene tetrads and triads flanked by ethylene units ($EP^r\underline{P}^r\underline{P}^rPE$ and $EP^r\underline{P}^rPE$) are present along with the syndiotactic pentads and hexads, we can conclude that the methyl signals of the comonomer sequences $P^rP^r\underline{P}^rP^rP$, $P^rP^r\underline{P}^rPE$ and $EP^r\underline{P}^rPE$ cannot be resolved. Therefore, in the copolymer, the substitution of the last P's on the two sides of the syndiotactic pentad does not give any detectable chemical shift variation.

Taking the signal of the syndiotactic propene pentad $P^rP^r\underline{P}^rP^rP$ as a reference chemical shift (18.13 ppm, resonance 15), the substitution of P adjacent to the central $\underline{P}$ on one side ($P^rP^r\underline{P}EP$, 18.01 ppm, resonance 17) gives an upfield shift of 0.12 ppm, while the substitution of the P in the same position on the other side ($PE\underline{P}EP$, 17.92 ppm, resonance 12) gives an upfield shift of 0.09 ppm.

Chart 1. Resonances of the Sequences Containing Inverted Propylene (Chemical Shifts in HMDS Scale)



The assignments of the resonances 17–19 are deduced from the intensity variation between the two samples of different composition and from the comparison with the intensities of the more resolved signals in the $S_{\alpha\alpha}$ region of the spectra (see Figure 3b and Table 5). The relatively wide signal at 17.96 ppm, that is noticeably intense even at low propene content, has been assigned to the unresolved pentads $\mathrm{P^rP^r\underline{P}EE}$ and $\mathrm{EP^r\underline{P}EE}$ (19). This assignment is in agreement with the fact that the syndiotactic diads and triads flanked by ethylene units give the most intense signals in the $S_{\alpha\alpha}$ region of the spectrum of the copolymer at low propene content.

The assignment of the $\mathrm{P^rP^r\underline{P}EP}$ (17) and $\mathrm{EP^r\underline{P}EP}$ (18) pentads is also performed according to the intensity variation. This assignment is only tentative due to the low signal resolution in this region.

The assignment of the isolated propene-centered pentads (12–14) is obviously the same as in the isotactic copolymer.

All these results show that in general the substitution of P with E produces, in syndiotactic propene methyl-centered sequences, much smaller chemical shift variations than in the isotactic sequences. There is a lack of information for sequences longer than pentads. Moreover, since the signals of the different comonomer pentads are very close, a quantitative evaluation is possible only for a few pentads.

In the copolymers prepared with the syndiospecific catalyst, signals due to the pentads containing isolated steric errors are also present and assigned in the downfield region between 18.70 and 18.49 ppm. The assignment of the resonances 10 and 11 is the same as in the isotactic copolymer. The assignment of the $\mathrm{EP^m\underline{P}^rPE}$ pentad (16) at 18.70 ppm has been performed by adding to the chemical shift of the pentad $\mathrm{P^mP^m\underline{P}^rPE}$ (assigned at 18.88 ppm according to the literature[14]) the upfield shift 0.18 ppm, produced by the substitution of P in the same position in the isotactic pentad $\mathrm{P^mP^m\underline{P}^mPE}$. This assignment agrees closely with the calculated chemical shift. If the $\mathrm{EP^m\underline{P}^rPE}$ pentad is present, the two corresponding $\mathrm{P^mP^r\underline{P}E\square}$ and $\mathrm{P^rP^m\underline{P}E\square}$ pentads should be present too. According to calculations, the chemical shift of the pentad $\mathrm{P^mP^r\underline{P}E\square}$ should be between 17.82 and 17.85 ppm (sequences 25 and 26 in Table 3 and Figure 2c). These signals are likely to be overlapped by the more intense resonances of the isolated propene-centered pentads. The assignment of the signal at 18.49 to the pentad $\mathrm{P^rP^m\underline{P}E\square}$ (20) agrees closely with the calculated chemical shift value.

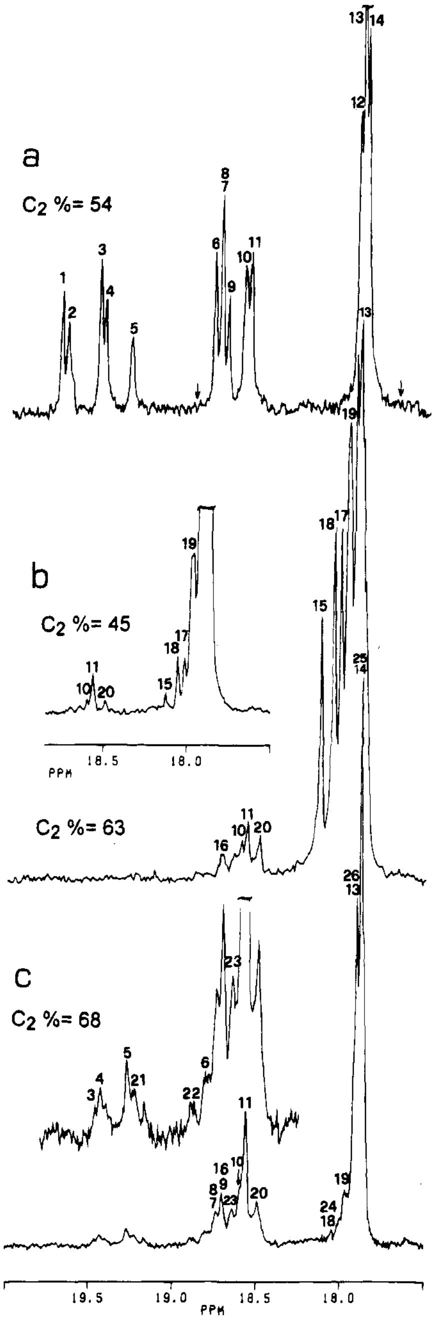


Figure 2. Expanded plot of the methyl region of ethylene–propylene copolymers prepared with isospecific (a), syndiospecific (b), and aspecific (c) catalysts.

Figure 2c shows the expanded plot of the methyl region of the copolymers prepared with the aspecific catalyst. In Table 3 the observed chemical shifts and assignments are given. The chemical shift differences, calculated by means of the CALMOD program, are given as well.

Here, besides the signals already assigned that are typical of the copolymers prepared with the isospecific and syndiospecific catalysts, only a few new signals of atactic propene-centered sequences are detected. Resonances 21–24 are assigned according to the literature.[14] The signal intensity of these pentads, that contain sequences of four propene units, is very low due to the

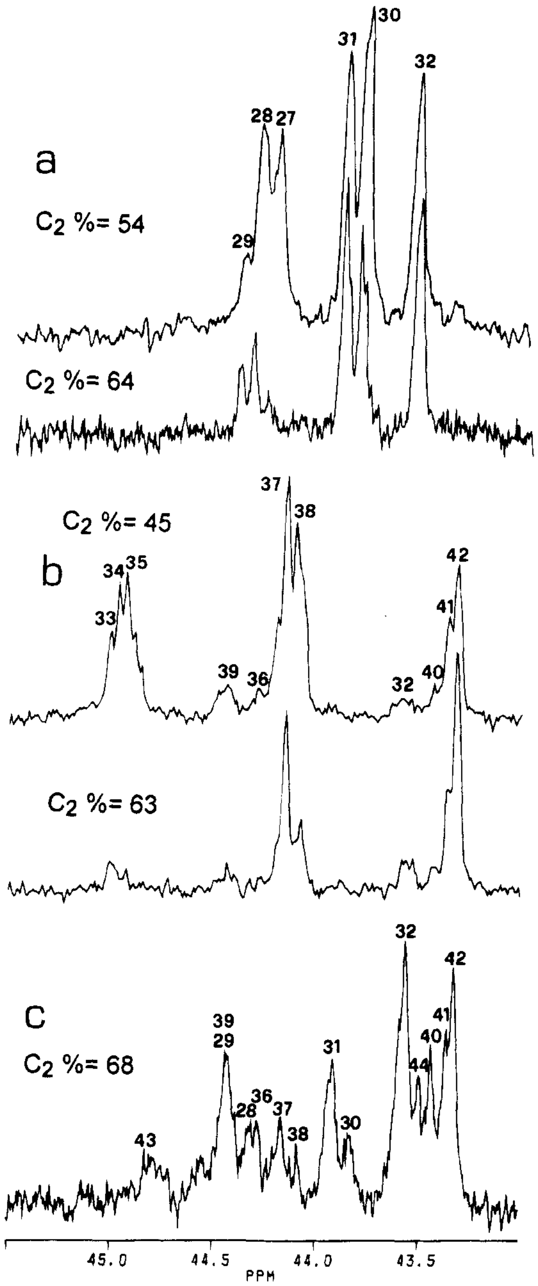


Figure 3. Expanded plot of the methylene $S_{\alpha\alpha}$ region of ethylene–propylene copolymers prepared with isospecific (a), syndiospecific (b), and aspecific (c) catalysts.

low propene content of the atactic copolymers observed.

The criteria adopted for the assignment of $EP^r\underline{P}^mPE$ (16), $P^rP^m\underline{P}E\square$ (20), and $P^mP^r\underline{P}E\square$ (25 and 26) pentads, that contain one isolated P^mP diad and are also present in the copolymer prepared with the syndiospecific catalyst, have been previously discussed.

Though many signals have been definitively assigned in the copolymer prepared with the aspecific catalyst, due to the overlapping of comonomer and tactic sequences, the quantitative evaluation of only a few pentads is possible.

Methylene $S_{\alpha\alpha}$ Region. Figure 3 shows the expanded plot of the methylene $S_{\alpha\alpha}$ region of the same copolymers. Figure 3a shows the expanded plot of the $S_{\alpha\alpha}$ region of the two copolymers of different compositions prepared with the isospecific catalyst. In Table 4 the observed chemical shifts and assignments are given. The chemical shift differences are compared with those observed in the literature.[9]

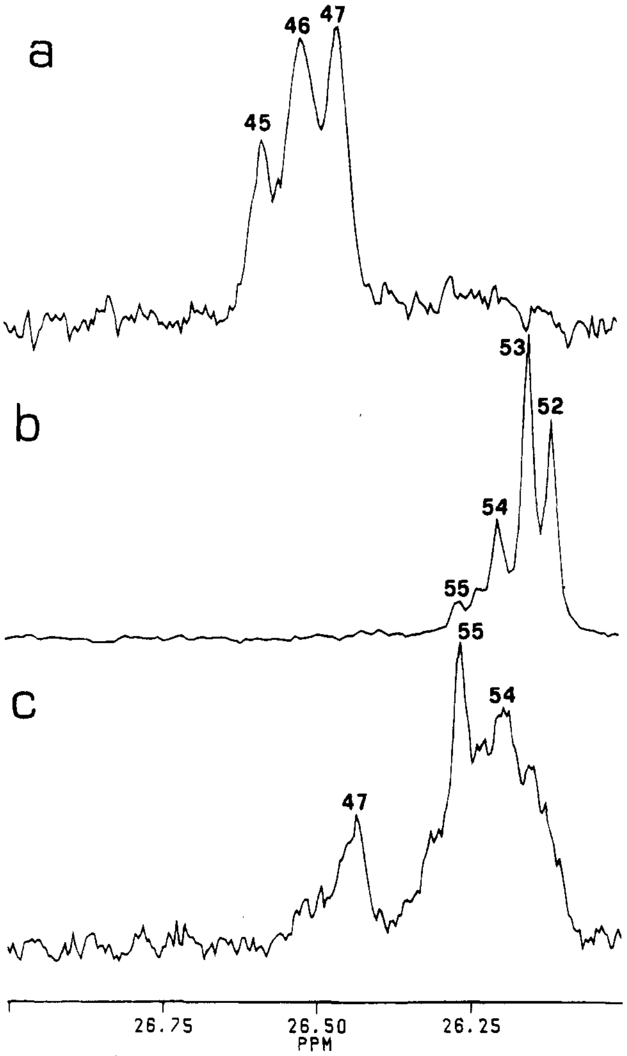


Figure 4. Expanded plot of the methine $T_{\beta\beta}$ region of ethylene–propylene copolymers prepared with isospecific (a), syndiospecific (b), and aspecific (c) catalysts.

The assignment of the isotactic propene hexad is performed by comparison with the spectrum of the isotactic homopolymer. The assignments of all other resonances are performed according to the intensity variations between the samples of different compositions. Taking the signal of the isotactic propene hexad as a reference chemical shift (44.23 ppm, resonance 27), we can observe that (i) the substitution of the first P's adjacent to the central $\underline{P}^m\underline{P}$ diad gives an upfield shift of 0.43 ppm on one side ($P^mP^m\underline{P}^m\underline{P}E\square$, 43.80 ppm, resonance 30) and of 0.25 ppm on the other side ($E\underline{P}^m\underline{P}E$, 43.55 ppm, resonance 32) and (ii) the substitution of the further P's ($P^mP^m\underline{P}^m\underline{P}^mPE$, 44.32 ppm, resonance 28; $EP^m\underline{P}^m\underline{P}^mPE$, 44.42 ppm, resonance 29) gives a downfield shift of 0.09 and 0.10 ppm, respectively.

After the substitution of the P's adjacent to the central $\underline{P}^m\underline{P}$ diad we cannot obtain any further information. As a consequence no more than three isotactic propene hexads are assigned and a quantitative evaluation of only the P^mP-centered tetrads can be given.

The fact that these chemical shift differences do not agree very closely with those observed in the literature could be due to the fact that the copolymer studied in the literature has a noticeably higher propene content.

Figure 3b shows the expanded plot of the $S_{\alpha\alpha}$ region of two copolymers of different compositions prepared

Table 3. Peak Assignment for the Methyl Region (Aspecific Catalyst)

carbon	sequence^a	no.	shift (ppm)	$\Delta\delta^b$ (ppm)	
				obsd	calcd^{c11}
$P_{\beta\beta}$	$P^mP^mP^m\underline{P}^mPE\square$	3	19.46		
	$EP^mP^m\underline{P}^mPE\square$	4	19.43	0.00	0.00
	$P^rP^m\underline{P}^mPE$	21	19.22	-0.21	-0.20
	$P^mP^m\underline{P}^rPE$	22	18.88	-0.55	-0.54
	$P^mP^r\underline{P}^mPE$	23	18.64	-0.79	-0.84
	$P^mP^r\underline{P}^rPE$	24	18.04	-1.39	-1.38
	$EP^m\underline{P}^mPE$	5	19.27		
	$EP^m\underline{P}^rPE$	16	18.70		
$P_{\beta\delta}$	$P^mP^mP^m\underline{P}EP\square$	6	18.80		
	$EP^mP^m\underline{P}EP\square$	7	18.74	0.00	0.00
	$P^mP^mP^m\underline{P}EE\square$	8	18.74	0.00	
	$EP^mP^m\underline{P}EE\square$	9	18.70	-0.04	-0.05
	$P^rP^m\underline{P}E\square$	20	18.49	-0.25	-0.22
	$P^mP^r\underline{P}EP$	25	17.87	-0.87	-0.92
	$P^mP^r\underline{P}EE$	26	17.90	-0.84	-0.89
	$P^rP^rPEE+EP^r\underline{P}EE$	19	17.96	-0.78	-0.66
	$EP^m\underline{P}EP$	10	18.59		
	$EP^m\underline{P}EE$	11	18.56		
	$EP^r\underline{P}EP$	18	18.04	-0.70	-0.69
$P_{\delta\delta}$	$PE\underline{P}EE$	13	17.90		
	$EE\underline{P}EE$	14	17.87		

[a] □ = E or P. [b] Chemical shift differences relative to the values of $EP^mP^m\underline{P}^mPE\square$ and $EP^mP^m\underline{P}EP\square$, respectively, which are set to be 0 ppm.

Table 4. Assignments for the $S_{\alpha\alpha}$ Region (Isospecific Catalyst)

sequence^a	no.	shift (ppm)	$\Delta\delta^b$ (ppm)	
			this work	lit.[9]
$P^mP^m\underline{P}^m\underline{P}^mP^mP$	27	44.23	0.00	0.00
$P^mP^m\underline{P}^m\underline{P}^mPE$	28	44.32	0.09	0.06
$EP^m\underline{P}^m\underline{P}^mPE$	29	44.42	0.19	0.46
$P^mP^m\underline{P}^m\underline{P}E\square$	30	43.80	-0.43	-0.41
$EP^m\underline{P}^m\underline{P}E\square$	31	43.91	-0.32	-0.19
$E\underline{P}^m\underline{P}E$	32	43.55	-0.68	-0.71

[a] □ = E or P. [b] Chemical shift differences relative to the value of $P^mP^m\underline{P}^m\underline{P}^mP^mP$, which is set to be 0 ppm.

with the syndiospecific catalyst. In Table 5 the observed chemical shifts and assignments are given.

The assignment of the $P^rP^r\underline{P}^r\underline{P}^rP^rP$ hexad is performed by comparison with the spectrum of a prevailingly syndiotactic homopolymer. The assignment of the other $\underline{P}^r\underline{P}$-centered sequences has been done according to the intensity variations between samples of different compositions.

Taking the signal of the syndiotactic propene hexad as a reference (44.93 ppm, resonance 35), we can observe that (i) the substitution of the first P's adjacent to the central $\underline{P}^r\underline{P}$ diad gives an upfield shift of 0.82 ppm on one side ($P^rP^r\underline{P}^r\underline{P}E\square$, 44.11 ppm, resonance 38) and of 0.75 ppm on the other side ($PE\underline{P}^r\underline{P}E\square$, 43.36 ppm, resonance 41) and (ii) the substitution of further P's gives a downfield shift of 0.04–0.05 ppm (see for instance the chemical shift difference between resonances 35 and 36 or between resonances 38 and 37).

In the copolymer prepared with the syndiospecific catalyst the $S_{\alpha\alpha}$ region is better resolved than the methyl region. Four hexads can be assigned, and a complete quantitative evaluation of the syndiotactic $\underline{P}^r\underline{P}$-centered sequences up to tetrads can be done.

Signals due to the tetrads containing isolated steric errors are present. The assignment of sequence 32 is the same as in the isotactic copolymer. Sequences 36, 39, and 40 are assigned according to calculations.

Figure 3c shows the expanded plot of the $S_{\alpha\alpha}$ region of a copolymer prepared with the aspecific catalyst. In Table 6 the observed chemical shifts and assignments

Table 5. Assignments for the $S_{\alpha\alpha}$ Region (Syndiospecific Catalyst)

sequence[a]	no.	shift (ppm)	$\Delta\delta^b$ (ppm) obsd	$\Delta\delta^b$ (ppm) calcd[11]
$EP^r\underline{P}^r\underline{P}^rPE$	33	45.01	0.00	0.00
$P^rP^r\underline{P}^r\underline{P}^rPE$	34	44.97	-0.04	*c*
$P^rP^r\underline{P}^r\underline{P}^rP^rP$	35	44.93	-0.08	*c*
$P^r\underline{P}^r\underline{P}^mP$	36	44.27	-0.74	-0.64
$EP^r\underline{P}^r\underline{P}E\square$	37	44.16	-0.85	-0.87
$P^rP^r\underline{P}^r\underline{P}E\square$	38	44.11	-0.93	-0.88
$P^r\underline{P}^m\underline{P}E$	39	44.44	-0.57	-0.62
$EP^m\underline{P}^r\underline{P}E\square$	40	43.43	-1.58	-1.49
$PE\underline{P}^r\underline{P}E\square$	41	43.36	-1.65	
$EE\underline{P}^r\underline{P}EE$	42	43.32	-1.69	-1.75
$E\underline{P}^m\underline{P}E$	32	43.56	-1.45	-1.55

[a] □ = E or P. [b] Chemical shift differences relative to the value of $EP^r\underline{P}^r\underline{P}^rPE$, which is set to be 0 ppm. [c] The values are unobtainable because of the limit in the program.

Table 6. Assignments for the $S_{\alpha\alpha}$ Region (Aspecific Catalyst)

tetrads	sequence[a]	no.	shift (ppm)	$\Delta\delta^b$ (ppm) obsd	$\Delta\delta^b$ (ppm) calcd[11]
$P\underline{PP}P$	$P^mP^m\underline{P}^m\underline{P}^mPE$	28	44.32	-0.11	*c*
	$EP^m\underline{P}^m\underline{P}^mPE$	29	44.43	0.00	0.00
	$P^m\underline{P}^m\underline{P}^rP$	43	44.80	0.37	0.41
	$P^m\underline{P}^r\underline{P}^rP$	36	44.27	-0.16	-0.14
$P\underline{PP}E$	$P^mP^m\underline{P}^m\underline{P}E\square$	30	43.83		
	$P^rP^r\underline{P}^r\underline{P}E\square$	38	44.08	0.00	0.00
	$PP^m\underline{P}^r\underline{P}E\square$	44	43.49	-0.59	-0.46
	$P^r\underline{P}^m\underline{P}E$	39	44.43	0.35	0.25
	$EP^m\underline{P}^m\underline{P}E\square$	31	43.91	0.00	0.00
	$EP^m\underline{P}^r\underline{P}E\square$	40	43.43	-0.48	-0.48
	$EP^r\underline{P}^r\underline{P}E\square$	37	44.16	0.25	0.14
$E\underline{PP}E$	$E\underline{P}^m\underline{P}E$	32	43.56		
	$PE\underline{P}^r\underline{P}E\square$	41	43.36		
	$EE\underline{P}^r\underline{P}EE$	42	43.33		

[a] □ = E or P; PP = P^mP or P^rP. [b] Chemical shift differences relative to the values of $EP^m\underline{P}^m\underline{P}^mPE$, $P^rP^r\underline{P}^r\underline{P}E\square$, and $EP^m\underline{P}^m\underline{P}E\square$, respectively, which are set to be 0 ppm. The chemical shift differences between the stereoisomers of the comonomer sequence $EP\underline{PP}E\square$. [c] Unobtainable because of the limit in the program.

are given. The calculated chemical shift differences are given as well. As in the case of the syndiotactic copolymer, the $S_{\alpha\alpha}$ signals, although noticeably broadened, are better resolved than the methyl signals. A few sequences up to tetrads and hexads can be not only assigned but also evaluated. Most signals have already been assigned in the copolymers made with isospecific and syndiospecific catalysts. Only two new resonances are detectable, one at 43.49 and the broadened one at 44.80 ppm, that are typical of the copolymer made with the aspecific catalyst. The assignment of such resonances to sequences 44 and 43, respectively, is done by taking into account the intensity variations between samples of different compositions (both resonances are detectable only in the copolymer at higher propene content) and the necessary relationships among the sequences. The assignments agree closely with calculations.

Methine Region. In Tables 7–9 the observed chemical shifts and assignments of methine carbons of the

Table 7. Assignments for the Methine Carbons (Isospecific Catalyst)

carbon	sequence[a]	no.	shift (ppm)
$T_{\beta\beta}$	$P^mP^m\underline{P}^mP^mP$	45	26.57
	$P^mP^m\underline{P}^mPE$	46	26.50
	$EP^m\underline{P}^mPE$	47	26.45
$T_{\beta\delta}$	$P^mP^m\underline{P}E\square$	48	28.64
	$EP^m\underline{P}EP$	49	28.59
	$EP^m\underline{P}EE$	50	28.64
$T_{\delta\delta}$	$E\underline{P}E$	51	31.01

[a] □ = E or P.

Table 8. Assignments for the Methine Carbons (Syndiospecific Catalyst)

carbon	sequence[a]	no.	shift (ppm)
$T_{\beta\beta}$	$PP^r\underline{P}^rPP$	52	26.11
	$PP^r\underline{P}^rPE$	53	26.15
	$EP^r\underline{P}^rPE$	54	26.20
	$EP^m\underline{P}^rPE$	55	26.27
$T_{\beta\delta}$	$P^rP^r\underline{P}E\square$	56	28.54
	$EP^r\underline{P}E\square$	57	28.51
$T_{\delta\delta}$	$E\underline{P}E$	51	31.01

[a] □ = E or P; PP = P^mP or P^rP.

Table 9. Assignments for the Methine Carbons (Aspecific Catalyst)

carbon	sequence[a]	no.	shift (ppm)
$T_{\beta\beta}$	$EP^m\underline{P}^mPE$	47	26.43
	$EP^m\underline{P}^rPE$	55	26.27
	$EP^r\underline{P}^rPE$	54	26.19
$T_{\beta\delta}$	$EP^m\underline{P}EE$	50	28.61
	$EP^r\underline{P}E\square$	57	28.51
$T_{\delta\delta}$	$E\underline{P}E$	51	31.01

[a] □ = E or P.

three copolymers are given. Figure 4 shows the expanded plot of the $T_{\beta\beta}$ region of the same copolymers. In the copolymer formed with the isospecific catalyst the isotactic pentad $P^mP^m\underline{P}^mP^mP$ is assigned by comparison with the spectrum of the corresponding homopolymer. As to the copolymer formed with the syndiotactic catalyst, it is not possible to distinguish the $P^rP^r\underline{P}^rP^rP$ and $P^mP^r\underline{P}^rP^rP$ pentads. Indeed, these two pentads are not resolved even in the spectrum of a prevailingly syndiotactic homopolymer, that contains about 15% isolated P^mP diad. Taking these signals as reference chemical shifts, the sequences derived from successive substitution of P with E are assigned by comparison of spectral intensities for samples of different compositions. As in the methyl region the substitution of the last P's of the pentads produces an upfield shift in the isotactic sequences and a downfield shift in the syndiotactic sequences.

For the copolymer formed with the isospecific catalyst, the analysis of the methine region does not supply any further information with respect to the methyl region that is much better resolved. The methine region is richer in information in the case of the copolymer formed with the syndiospecific catalyst. Here, in fact, it is possible to distinguish and to quantitatively evaluate the $EP^r\underline{P}^rPE$ pentad (54) that, in the methyl region, is unresolved with the $P^rP^r\underline{P}^rP^rP$ and $EP^r\underline{P}^rP^r$ pentads. Signal 55, which is the most intense peak in the atactic copolymer and is also present in the syndiotactic copolymer, is assigned to the $EP^m\underline{P}^rPE$ pentad. In the copolymer formed with the aspecific catalyst, it is not possible to assign longer atactic sequences, due to the low propene content and to the breadth of the resonances.

Experimental Section

The ethylene–propylene copolymers studied here have been prepared with homogeneous isospecific, syndiospecific, and aspecific metallocene-based Ziegler–Natta catalysts. The samples prepared with the isospecific catalyst contain 54 and 64 mol % ethylene. The samples prepared with the syndiospecific catalyst contain 45, 55, and 63 mol % ethylene. The samples prepared with the aspecific catalyst contain 68 and 78 mol % ethylene.

The polymer composition of the samples prepared with the isospecific catalyst was calculated from the dyad distribution (methylene peaks) and triad distribution (methyl and methylene peaks and methine and methylene peaks).[6] The three methods are in good agreement. The polymer composition of the samples prepared with the syndiospecific and aspecific catalysts was calculated from the dyad distribution (methylene peaks).

Chemical shift calculations have been performed by using Cheng's CALMOD computer program,[11] kindly provided by the author. In the calculation one more E unit is added to both sides of the considered sequence; e.g., for the sequence PPPEP actually EPPPEPE is calculated to get the chemical shift of the central unit. Each set of chemical shift differences is expressed relative to the peak of a similar sequence, containing the highest number of propene units and having the highest stereoregularity, which is set to be 0 ppm.

All the spectra were obtained by using a Bruker AM-270 spectrometer operating at 67.89 MHz in the PFT mode, at a temperature of 107 °C. The samples were dissolved in $C_2D_2Cl_4$, using HMDS as an internal chemical shift reference. In all measurements CPD was used to remove $^{13}C-^{1}H$ couplings, the pulse angle was 90°, the pulse repetition time was 27 s, and 4500 free induction decays were stored in 32 000 data points using a spectral window of 4950 Hz.

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