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A Study of the Dispersity of Catalytic Sites in Ethylene/Propylene Copolymerization Through Computer-Assisted ^{13}C NMR Analysis

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A series of ethylene(*E*)/propylene(*P*) copolymers covering a large range of compositions is obtained by a new solution copolymerization process. The catalyst system consists of a high-activity, high-regioselectivity and high-stereospecificity *Ti* complex supported on MgCl_2 . The cocatalyst is triethylaluminum treated with diphenyldimethoxysilane. The polymers are studied by ^{13}C NMR, and the *E*- and *P*-centered triads analyzed via the computer-assisted analytical approach. Through a systematic analysis, one can determine the minimum number of components that are needed to fit the data. Each component would correspond to a family of similar catalytic sites. The reactivity ratios (r_E and r_P) of each family of active sites and the component weight factor (related to the catalytic activity) are also determined.

KEY WORDS Dispersity of catalytic sites, ethylene-propylene copolymers, ^{13}C NMR characterization, computer-assisted analysis.

INTRODUCTION

NMR has often been used to derive detailed structural and mechanistic information on polyolefins. A major difficulty in such studies is the heterogeneous nature of the Ziegler-Natta catalysts. These catalysts contain multiple catalytic sites and produce polymers that comprise multiple components. Each component, in turn, may differ in comonomer sequence distribution and in tacticity. The observed NMR spectrum of such a polymer rep-

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resents the sum of the contributions from all the components and is, in general, difficult to interpret. Recently, analytical methodologies [1–4] have been developed with the aid of computers that enable the NMR data of such multicomponent polymers to be studied.

There are technical problems in preparing ethylene(*E*)/propylene(*P*) copolymers that cover a wide range of compositions under the same experimental conditions. Reactivity ratios are meaningless if the propagation reaction is diffusion-controlled [5]. In order to avoid diffusion control, it is often necessary to keep the reaction system to one polymer phase. Thus, if the polymerizing medium consists of a mixture of a solid polymer and a viscous solution, diffusion control may occur, leading to a decrease in the polymerization rate and a change in copolymer composition, as monomers with different sizes will diffuse with different diffusion constants. Slurry polymerization only permits the synthesis of copolymers with low ethylene content (less than 5 mol %). At compositions higher than 7–8 mol %, the copolymers tend to be soluble in the diluent. If a series of copolymers is made containing low and high ethylene levels, the kinetics of polymerization for polymers that are insoluble in the diluent would be reaction-controlled, whereas the kinetics for polymers soluble in the diluent may be diffusion-controlled. If one observes the variations in the reactivity ratios for this series of copolymers, the trends would not be meaningful. Gas phase polymerization is also problematical because the copolymers with 50 mol % composition are sticky elastomers and are difficult to handle under controlled conditions.

We have developed a solution copolymerization process that bypasses these problems. In this work, a series of E/P copolymers covering a large range of composition is obtained by this new solution copolymerization process where the comonomer feed is kept constant throughout the polymerization. The catalyst system consists of a high-activity stereospecific *Ti* complex supported on MgCl₂. The cocatalyst is triethylaluminum treated with diphenyldimethoxysilane [6]. The polymers are analyzed by ¹³C-NMR and the average *E*- and *P*-centered triads are computed.

The computer-assisted analytical approach [4] is then used to analyze the NMR triad data. Through a systematic study, one can determine the minimum number of components that are needed to fit the data. Each component would correspond to a family of similar catalytic sites. The reactivity ratios (r_E and r_P) of each family of active sites and the component weight factor (related to the catalytic activity) are also determined via this computer-assisted method.

EXPERIMENTAL

Copolymer Synthesis

The copolymer synthesis is performed in a 1-L stainless-steel stirred reactor at 70°C using 500 mL pure anhydrous toluene as solvent. The catalyst (10 to 20 mg) comprises a conventional solid component (magnesium chloride-dibutylphthalate-titanium tetrachloride) associated with a cocatalyst mixture: triethylaluminum (6mM) + diphenyldimethoxysilane (0.3 mM). A total pressure of 4 bars (including 0.1 bar H₂) is maintained throughout the polymerization time (1.5 h) by continuous addition of a constant monomer feed, an ethylene-propylene mixture corresponding to the desired copolymer composition. After polymerization, the polymers (60 to 100g) are recovered by methanol precipitation.

The monomer ratio in the solution is defined by the monomer mixture added to the gas phase and depends also on the solubilities of the monomer in the range of temperature used. The solubility of propylene is about 12 g/L/bar of partial propylene pressure. The corresponding value for ethylene is about 2 g/L/bar of partial ethylene pressure. The mole ratio of propylene to ethylene is then four times larger in the solution than in the gas phase.

Two assumptions are implicit in the analysis. First, the monomer ratio in the reactor (for a given sample) is assumed to be constant for the entire time of polymerization. This is shown to be valid by the fact that the copolymer composition is found to be nearly equal to the composition of the monomer feed added to the reactor. (Slightly larger discrepancy is observed for samples 6, 9 and 10, as shown in Table I.) Secondly, the methanol precipitation recovered most of the polymers. The amounts of methanol soluble polymers are found to be negligible.

NMR Spectra

The ^{13}C -NMR spectra were recorded on a Bruker AC 250 spectrometer at 62.9 MHz. Polymer samples were examined as 10% (w/v) solutions. A mixture of tetrachloroethylene (TCE) and perdeuterobenzene (C_6D_6) (2/1 by volume) was used as the solvent [7]. Chemical shift values (δ) are given in ppm in reference to internal tetramethylsilane (TMS); the chemical shift of TCE is 120.75 ppm. Spectra were obtained with a broad band/ ^1H dual 10-mm probe. The probe temperature was set at 365 K. Typical accumulation conditions included: 70° rf pulse, spectral width 8500 Hz (135 ppm), 10-s recycle time to allow for complete relaxation, and about 1000–5000 scans. Intensities of the resonances were determined by planimetric measurements after suitable enlargement. No significant difference in relative intensities, for the carbons of interest to us, was observed between acquisitions made under these conditions and those made in the absence of the nuclear Overhauser effect (N.O.E.).

TABLE I

Composition of the monomer feed added to the reactor (1) and in the solution (2) and average composition of the polymer in % mole ethylene

| Sample No. | Ethylene content: % mol (E)/(E) + (P) | | |
|------------|---------------------------------------|---|---------------------|
| | (1) monomer feed added to the reactor | (2) monomer concentration in the solution | polymer composition |
| 1 | 2 | 0.5 | 2.10 |
| 2 | 8 | 2.0 | 7.35 |
| 3 | 10 | 2.7 | 9.15 |
| 4 | 15 | 4.2 | 12.75 |
| 5 | 20 | 5.9 | 21.80 |
| 6 | 25 | 7.7 | 31.00 |
| 7 | 35 | 11.8 | 36.30 |
| 8 | 35 | 11.8 | 38.15 |
| 9 | 50 | 20.0 | 45.70 |
| 10 | 58 | 25.6 | 63.40 |

RESULTS AND DISCUSSION

The solution copolymerization process we have developed bypasses the technical difficulty of obtaining ethylene/propylene copolymers that cover a large range of composition under experimental conditions permitting a clean control of the reaction. Whereas isotactic polypropylene is rather difficult to dissolve in aromatic solvents at low temperatures, we have observed that polypropylene prepared in an aromatic solvent at a high temperature remains in solution at temperatures above 65°C, even when the polymer has high molecular weight and high isotacticity. We have taken advantage of this observation and prepared copolymers in hot toluene covering a wide range of composition (0–60 mol % ethylene). An ethylene content much higher than 60 mol % would give a copolymer fraction insoluble in the solvent.

In reactions of this type, side reactions with toluene (e.g., Friedel-Craft type) are expected to occur and have discouraged the use of solution polymerization in industrial processes in the past. In the case of superactive third-generation supported Ziegler-Natta catalysts, these side reactions are absent because the concentrations of Lewis acids used with these catalysts are very low. For propylene homopolymerization, the activities and the stereospecificities are found to be the same for polymerizations either in heptane slurry or in toluene solution.

NMR Results

A typical ^{13}C -NMR spectrum is given in Figure 1. Peaks assignments are given in Table II; there are only slight differences in chemical shift values observed here in TCE/C $6\text{D}6$ compared with previous results in 1,2,4-trichlorobenzene/C $6\text{D}6$. The terminology and assignments used are those published by Carman *et al.* [8] and Cheng [9]: *t*, *p* and *s* refer

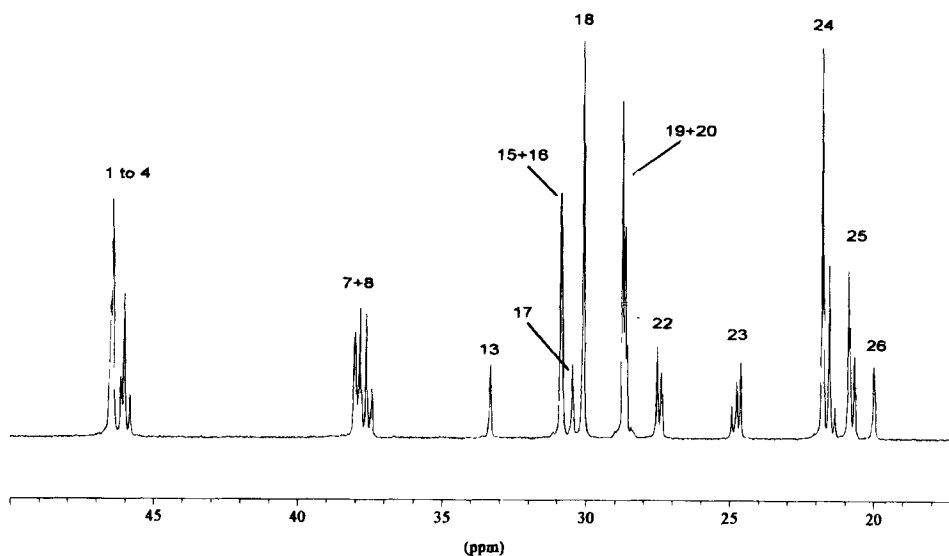


FIGURE 1 ^{13}C -NMR spectrum of ethylene/propylene copolymer, sample 7

TABLE II

¹³C-NMR assignments of ethylene/propylene copolymers in TCE/C₆D₆
(2/1 by volume) at 365K

| No | δ , ppm | carbon | remark |
|-------|------------------------|--------------------------------------|-----------------|
| 1-4 | 48.1-45.3 | $S_{\alpha\alpha}$ | |
| 5 | 38.8 | $S_{\alpha\gamma}$ | r- conf. |
| 6 | 38.45 | $S_{\alpha\delta}$ | r- conf. |
| 7 | 38.00, 37.85 | other $S_{\alpha\gamma}$ | m-conf. + i |
| 8 | 37.60, 37.45 | other $S_{\alpha\delta}$ | m-conf. + i |
| 9 | n.d. | $S_{\alpha\beta}$ | r-conf. + i |
| 10 | 34.95 | other $S_{\alpha\beta}$ | m-conf. + i |
| 11 | n.d. | $T_{\gamma\gamma}$ | i |
| 12 | n.d. | $T_{\gamma\delta}$ | i |
| 13 | 33.30 | $T_{\delta\delta}$ | |
| 14 | n.d. | $T_{\beta\gamma}$ | i |
| 15+16 | 30.85 | $S_{\gamma\gamma} + T_{\beta\delta}$ | |
| 17 | 30.45 | $S_{\gamma\delta}$ | |
| 18 | 30.05 | $S_{\delta\delta}$ | |
| 19 | 28.65 | $T_{\beta\beta}$ | m-m-PPP |
| 20 | 28.45 | $T_{\beta\beta}$ | mr-PPP + rr-PPP |
| 21 | 27.90 | $S_{\beta\gamma}$ | i |
| 22 | 27.50, 27.35 | $S_{\beta\delta}$ | |
| 23 | 24.95, 24.75, 24.60 | $S_{\beta\beta}$ | |
| 24 | 22.0-21.15 | $P_{\beta\beta}$ | mm-PPP |
| 25 | 21.15-20.35 | $P_{\beta\beta}$ | mr-PPP |
| | | $P_{\beta\gamma} + P_{\beta\delta}$ | m-i + m-PPE |
| 26 | 20.35-19.6 | $P_{\beta\beta}$ | rr-PPP |
| | | $P_{\beta\gamma} + P_{\beta\delta}$ | r-i + r-PPE |
| | | $P_{\gamma\gamma}$ | EPE |

respectively to tertiary (methine), primary (methyl) and secondary (methylene) carbons. The Greek subscripts refer to the distance a given carbon is from neighboring methine carbon bearing a methyl group; the letters *m* and *r* refer to meso and racemic propylene diads. Two other useful notations are added: the letter *i* refers to resonances coming from inverted propylene placement, and the peak numbers from inverted microstructures are underlined.

Composition of Copolymers

Because there is overlap of the resonances due to $T_{\beta\delta}$ and $S_{\gamma\gamma}$ [peaks (15) + (16)], the intensity corresponding to $S_{\gamma\gamma}$ is calculated as follows:

$$(S_{\gamma\gamma}) = 1/2 \{(S_{\beta\delta}) - (S_{\gamma\delta})\} = 1/2 \{(22) - (17)\};$$

$$(S_{\gamma\gamma}) = 1/2 \{(S_{\alpha\delta}) - (S_{\gamma\delta})\} = 1/2 \{(8) - (17)\}.$$

The mean value of $S_{\gamma\gamma}$ using the above two equations is used. The intensity of $T_{\beta\delta}$ is then calculated as (15) + (16) - ($S_{\gamma\gamma}$). In this section, numbers and sequence notations in parentheses correspond to the intensities of those peak numbers and sequences.

In order to check the quantitation of the NMR data obtained without N.O.E. suppression and under the experimental conditions described above, we compared the following intensities: (1) the sum of the tertiary carbons (all relative to *P* units) called *r*; (2) the sum of the primary carbons (all relative to *P* units) called *p*; (3) the part of the total secondary carbons

(*s*) equal to the number of *P* units and called *s(P)*. These determinations are based on the following relationships:

$$\begin{aligned}
 t &= (\underline{11}) + (\underline{12}) + (13) + (\underline{14}) + (15) + (16) - (S_{\gamma\gamma}) + (19) + (20) \\
 p &= (24) + (25) + (26) \\
 s &= (1) + (2) + (3) + (4) + (5) + (6) + (7) + (8) + (\underline{9}) + (\underline{10}) + \\
 &\quad (17) + (18) + (\underline{21}) + (22) + (23) + (S_{\gamma\gamma})
 \end{aligned}$$

The quantity *s(P)* can be readily calculated because each *P* unit (normal and inverted insertion) has two methylene carbons in the α position ($\alpha\beta$, $\alpha\gamma$, or $\alpha\delta$) except for the internal $\alpha\alpha$ carbon of a head-to-tail *PP* diad. The following equation then holds:

$$\begin{aligned}
 s(P) &= (1) + (2) + (3) + (4) + \frac{1}{2}\{(5) + (6) + (7) + (8) + (9) + (10)\} \\
 (E)/\{(E) + (P)\} &= \{s - s(P)\}/\{s + s(P)\} && \text{sec} - \text{sec} \\
 (E)/\{(E) + (P)\} &= \{s - t\}/\{s + t\} && \text{tert} - \text{sec} \\
 (E)/\{(E) + (P)\} &= \{s - p\}/\{s + p\} && \text{prim} - \text{sec}
 \end{aligned}$$

The ratios obtained for *s(P)/t*, *s(P)/p* and *p/t* are given in Table III; the agreement among them is excellent (nearly equal to 1). Nevertheless, slight differences are found between the composition values (mol % ethylene) obtained via the three different equations. The determination using secondary carbons is preferred as it is independent of possible N.O.E. differences between the different types of carbons.

Inverted Propylene Insertion

Resonances typical of inverted insertion of propylene units in the chain include peaks (9), (10) and (21) (secondary carbons *S*) and (11), (12) and (14) (tertiary carbons *T*). These inverted sequences also complicate the methyl carbons assignments. In the samples studied, these resonances corresponding to propylene inversion are not detected except in sample 10 where, surprisingly, peak 12 is about 1.10% of the total tertiary carbons. Except in this case, it can be concluded that the catalyst is highly regioselective.

TABLE III
Polymer composition (% mol *E*) calculated from ^{13}C -NMR data after comparison between intensities of the different carbons related to propylene units [*p*, *t* and *s(P)*]

| No. | consistency tests | | | % mol ethylene, (E)/{(E) + (P)} | | |
|-----|-------------------|---------------|------------|---------------------------------|--------------|--------------|
| | <i>s(P)/t</i> | <i>s(P)/p</i> | <i>p/t</i> | sec. - sec. | tert. - sec. | prim. - sec. |
| 1 | 0.963 | 1.059 | 1.004 | 2.10 | 1.90 | 3.50 |
| 2 | 0.990 | 0.967 | 1.024 | 7.35 | 6.85 | 5.70 |
| 3 | 1.004 | 1.009 | 0.995 | 9.15 | 9.35 | 9.60 |
| 4 | 0.950 | 0.947 | 1.003 | 12.75 | 10.25 | 10.10 |
| 5 | 0.985 | 1.024 | 0.962 | 21.80 | 21.10 | 22.95 |
| 6 | 0.945 | 0.950 | 0.995 | 31.00 | 28.40 | 28.65 |
| 7 | 1.008 | 0.975 | 1.034 | 36.30 | 36.65 | 35.20 |
| 8 | 1.037 | 0.990 | 1.048 | 38.15 | 39.70 | 37.70 |
| 9 | 1.036 | 0.987 | 1.050 | 45.70 | 47.15 | 45.20 |
| 10 | 1.011 | 0.998 | 1.013 | 63.40 | 63.70 | 63.35 |

Tacticity

Very high isotacticity of these polymers is indicated by the very weak or zero intensities of resonances (5) and (6) in all the samples. Carbon resonances from *PPP(mm)* and *PPP(mr+rr)* previously assigned by Cheng [9] at 90 MHz to peaks (19) and (20), respectively, overlap at 62.9 MHz. Nevertheless, the ratio (*mm-PPP*)/(total *PPP*) can be estimated in the following way.

First, one can calculate the ratio of *PPP* triads among the total *P*-centered triads:

$$\tau = (PPP) / \{(PPP) + (PPE) + (EPE)\}$$

One can then determine τ' , where $\tau' = (24) / \{(24) + (25) + (26)\}$. Owing to the very low level of propylene inversion, τ' is nearly equal to $(mm-PPP) / \{(PPP) + (PPE) + (EPE)\}$. Thus, τ'/τ gives an estimate of the isotactic *mm-PPP* triads among the total *PPP* triads.

Using the equations above, we obtain very high isotactic values for the polymers. For example, samples 1, 2, 3 and 4 have the following (*mm*) contents: 99.4, 1.00, 99.2, and 99.4%, respectively.

Copolymer Triad Distribution

The *P*-centered triads can be readily calculated as follows:

$$(EPE) = (T_{\delta\delta}) = (13)$$

$$(PPE) = (T_{\beta\delta}) = (15) + (16) - (S_{\gamma\gamma})$$

$$(PPP) = (T_{\beta\beta}) = (19) + (20)$$

$$(\text{other } P\text{-centered triads}) = (T_{\gamma\gamma}) + (T_{\gamma\delta}) + (T_{\beta\gamma}) = (11) + (12) + (14)$$

The last equation is a consequence of inverted propylene insertions and not the true amount of inversions present. In fact each inversion may generate up to three irregular tertiary carbons, so that other *P*-centered triads may be up to three times the amount of inversions.

The *E*-centered triads can be calculated via the equations below:

$$(PEP) = (S_{\beta\beta}) = (23)$$

$$(PEE) = (S_{\beta\delta}) = (22)$$

$$(EEE) = \frac{1}{2}(S_{\delta\delta}) + \frac{1}{4}(S_{\gamma\delta}) = \frac{1}{2}(18) + \frac{1}{4}(17)$$

(other *E*-centered units) = $\frac{1}{2}(S_{\beta\gamma}) + \frac{1}{4}(S_{\alpha\beta}) = \frac{1}{2}(21) + \frac{1}{4}\{(9) + (10)\}$. Again the last equation is a consequence of the inversion of propylene and derives from the following expression:

$$(\text{other } E\text{-centered triads}) = \frac{1}{2}s(E) - (PEP) - (PEE) - (EEE),$$

where $S(E) = s - s(P)$.

The triad intensities calculated using the above equations are summarized in Table IV. The *P*-centered triads and the *E*-centered triads have been separately normalized to 100%.

TABLE IV

Triad distribution in the copolymer from ^{13}C -NMR data. Propylene insertion is mostly regioregular. "Others" includes the contribution from regioirregular sequences

| % mole ethylene | | % P centered triads | | | | % E centered triads | | | |
|-----------------|---------|---------------------|-------|-------|--------|---------------------|-------|-------|--------|
| No. | polymer | PPP | PPE | EPE | others | EEE | EEP | PEP | others |
| 1 | 2.10 | 96.30 | 3.50 | 0.20 | — | 7.00 | 14.65 | 78.35 | — |
| 2 | 7.35 | 87.60 | 11.50 | 0.90 | — | 7.05 | 19.65 | 73.30 | — |
| 3 | 9.15 | 85.05 | 13.55 | 1.40 | — | 10.15 | 22.40 | 67.45 | — |
| 4 | 12.75 | 82.05 | 16.15 | 1.80 | — | 11.65 | 25.10 | 63.25 | — |
| 5 | 21.80 | 79.05 | 16.85 | 3.90 | 0.20 | 43.30 | 24.15 | 32.55 | — |
| 6 | 31.00 | 68.30 | 24.65 | 7.05 | — | 37.90 | 31.65 | 30.40 | — |
| 7 | 36.30 | 58.60 | 31.30 | 9.85 | 0.25 | 38.35 | 32.00 | 29.65 | — |
| 8 | 38.15 | 60.45 | 29.10 | 10.45 | — | 46.70 | 28.70 | 24.60 | — |
| 9 | 45.70 | 47.00 | 37.75 | 15.25 | — | 41.50 | 34.55 | 23.95 | — |
| 10 | 63.40 | 38.00 | 36.10 | 24.80 | 1.10 | 62.00 | 26.20 | 11.80 | 0.75 |

NMR Data and Catalytic Sites

In principle, an ethylene-propylene copolymer, with the occurrence of propylene tacticity and inversion, should be considered a five-component copolymer. However, the following characteristic features of the polymer series studied here permit a simpler treatment to be made: 1) regioregular insertion, 2) high isotacticity, 3) absence of compositional drift in the solution during the polymerization.

Owing to the constant monomer feed, the instantaneous comonomer feed concentrations are constant throughout the polymerization process and equal to the overall polymer composition; this is also true for the copolymer diad and triad distribution.

Different models can be used for the analysis of data:

Single-component first-order Markovian model

The following values can be obtained readily from NMR data.

$$R_p = \frac{(EPP)/2}{(EPE)} = \frac{(PPP)}{(PPE)/2} = \frac{(PP)}{(PE)/2}$$

$$R_e = \frac{(PEE)/2}{(PEP)} = \frac{(EEE)}{(EEP)/2} = \frac{(EE)}{(EP)/2}$$

In addition, we can define the following values

$$C_p = (PPE)^2/4 \times (EPE) \times (PPP) = 1$$

$$C_e = (EEP)^2/4 \times (PEP) \times (EEE) = 1$$

Both C_p and C_e are equal to 1 and the system can be described by one family of sites characterized by two reactivity ratios r_E and r_P

$$r_P = R_p (f_E/f_P), \text{ and } r_E = R_e (f_P/f_E)$$

where f_E/f_P is the monomer feed ratio in the solution. These reactivity ratios are calculated based on the well-established relations between triad distribution and reactivity ratios [10].

A special case corresponding to $r_E \cdot r_P = 1$ is detectable by the relationship, $R_p \cdot R_e = 1$ (easily calculated from the NMR data). This is the Bernoullian model where copolymerization is ideal, and the nature of the last monomer residue on the propagating chain has no influence on the relative rates of addition of the monomers.

Single-component second-order Markovian model

Equivalent probability ratios can be defined:

$$R_{ep} = \frac{(EPP)/2}{(EPE)}; \quad R_{pp} = \frac{(PPP)}{(PPE)/2}$$

$$R_{pe} = \frac{(PEE)/2}{(PEP)}; \quad R_{ee} = \frac{(EEE)}{(EEP)/2}$$

Then $C_p = R_{ep}/R_{pp}$ and $C_e = R_{pe}/R_{ee}$. In this case both C_p and C_e are not equal to 1 and the system can be described by a one-component model with four reactivities and the insertion of the monomer depends not only on the terminal monomer residues but also the penultimate monomer residues. The reactivity ratios are given as follows:

$$r_{EP} = R_{ep} (f_E/f_P), \quad \text{and} \quad r_{PP} = R_{pp}/C_p$$

$$r_{PE} = R_{pe} (f_P/f_E), \quad \text{and} \quad r_{EE} = R_{ee}/C_e$$

Multiple-component model

The single-component second-order Markovian model is one way to explain the situation where C_p and $C_e \neq 1$. Other hypotheses can also be formulated. One reasonable hypothesis for our situation is to suppose that: 1) there are more than one family of active sites, and 2) in Ziegler-Natta catalysis the relative rates of insertion of the monomers are not influenced by the last insertion, and $r_E \cdot r_P = 1$ is true for each site. Thus, each type of catalytic site κ is characterized by two reactivity ratio $r_{E,\kappa}$ and $r_{P,\kappa}$ with $r_{E,\kappa} \cdot r_{P,\kappa} \approx 1$ and the coexistence of different types of catalytic sites gives different types of polymer chains with:

$$\frac{[(EPP)/2]_{\kappa}}{[(EPE)]_{\kappa}} = \frac{[(PPP)]_{\kappa}}{[(PPE)/2]_{\kappa}} = R_{P,\kappa} = r_{P,\kappa} \cdot f_P/f_E.$$

In the whole (nonfractionated) polymer,

$$\frac{(EPP)/2}{(EPE)} = \frac{\sum_{\kappa} [(EPP)/2]_{\kappa}}{\sum_{\kappa} [(EPE)]_{\kappa}}.$$

With $\sum [(EPP)/2]_{\kappa} = (f_P/f_E) \sum [(EPE)]_{\kappa} \cdot r_{P,\kappa}$, then

$$\frac{(EPP)/2}{(EPE)} = f_P/f_E \cdot \frac{\sum_{\kappa} [(EPE)/2]_{\kappa} \cdot r_{P,\kappa}}{\sum_{\kappa} [(EPE)]_{\kappa}}; \quad \text{and}$$

$$\frac{(PPP)/2}{(PPE)} = f_P/f_E \cdot \frac{\sum_{\kappa} [(PPE)/2]_{\kappa} \cdot r_{P,\kappa}}{\sum_{\kappa} [(PPE)]_{\kappa}}.$$

If there is more than one family of sites, then

$$\frac{(EPP)/2}{(EPE)} \neq \frac{(PPP)}{(PPE)/2}, \quad \text{and} \quad C_p, C_e \neq 1.$$

From the NMR data, we can calculate C_p and C_e values. In our sample series, both values are much lower than 1, as shown in Table V. We obviously do not have a single-component, first-order Markovian case. Further analysis is possible through a computer-aided methodology.

Analysis through Computer-aided Methodology

The normalized triad data given in Table IV are converted on the overall triad basis, taking into account the copolymer composition. The triad intensities which come from inverted propylene insertion are ignored. The analysis is done in a systematic fashion, consisting of three steps.

Single sample analysis

The triad data of each sample are analyzed separately in order to determine whether the samples contain multiple components [2]. This has been done with a one-component first-order Markovian (**M1**) model and a two-component model involving Bernoullian (**B**) statistics. In the latter model (two-state **B/B**), two components are assumed to be present with a weight factor w_κ and reactivity ratio $r_{E,\kappa}$ (and $r_{P,\kappa} = 1/r_{E,\kappa}$) for each component. This is readily done using program FITCO/TRIAD [2] and program MIXCO/TRIAD [11]. The results are given in Table VI in which P_{EP} and P_{PE} are the first-order Markovian probabilities, and P_P is the Bernoullian probability of propylene enchainment, and w_κ is the component weight factor.

From Table VI, it appears that all the samples contain multiple components. The mean deviations for the two-state **B/B** model are all much smaller than the one-state **M1** model. The key information here is the values of $P_{P,\kappa}$. By use of the f_E/f_P ratio, the reactivity ratios corresponding to the $P_{P,\kappa}$ values can be calculated. The reactivity ratio for ethylene ($r_{E,\kappa}$) are shown on the right side of Table VI. Because the Bernoullian model is assumed, the reactivity ratio of propylene ($r_{P,\kappa}$) is simply equal to $1/r_{E,\kappa}$.

TABLE V

C_p and C_e values obtained directly from NMR data as a simple and characteristic feature of the catalyst system

| No. | mol % ethylene, in polymer | C_e | C_p |
|-----|-------------------------------|-------|-------|
| 1 | 2.10 | 0.100 | 0.165 |
| 2 | 7.35 | 0.190 | 0.430 |
| 3 | 9.15 | 0.185 | 0.395 |
| 4 | 12.75 | 0.215 | 0.444 |
| 5 | 21.80 | 0.105 | 0.230 |
| 6 | 31.00 | 0.215 | 0.315 |
| 7 | 36.30 | 0.225 | 0.425 |
| 8 | 38.15 | 0.180 | 0.335 |
| 9 | 45.70 | 0.300 | 0.495 |
| 10 | 63.40 | 0.235 | 0.345 |

TABLE VI
Analysis of triad data of individual samples

| No. | M1 Model ^a | | | Two-state (B/B) model ^b | | | | | | |
|-----|-----------------------|----------|-----------------|------------------------------------|-------|-----------|-------|-----------------|-----------|-----------|
| | P_{PE} | P_{EP} | MD ^c | $P_{P,1}$ | w_1 | $P_{P,2}$ | w_2 | MD ^c | $r_{E,1}$ | $r_{E,2}$ |
| 1 | 0.019 | 0.892 | 0.097 | 0.136 | 0.005 | 0.982 | 0.995 | 0.085 | 1264 | 3.7 |
| 2 | 0.066 | 0.879 | 0.281 | 0.311 | 0.014 | 0.938 | 0.986 | 0.205 | 109 | 3.2 |
| 3 | 0.080 | 0.843 | 0.467 | 0.429 | 0.049 | 0.931 | 0.951 | 0.058 | 48 | 2.7 |
| 4 | 0.103 | 0.825 | 0.767 | 0.406 | 0.067 | 0.914 | 0.933 | 0.231 | 33 | 2.2 |
| 5 | 0.134 | 0.640 | 2.919 | 0.181 | 0.171 | 0.907 | 0.829 | 0.207 | 72 | 1.6 |
| 6 | 0.206 | 0.612 | 3.209 | 0.241 | 0.264 | 0.860 | 0.736 | 0.211 | 38 | 2.0 |
| 7 | 0.229 | 0.388 | 2.730 | 0.218 | 0.280 | 0.802 | 0.720 | 0.277 | 27 | 1.8 |
| 8 | 0.214 | 0.328 | 2.939 | 0.192 | 0.331 | 0.822 | 0.669 | 0.303 | 32 | 1.6 |
| 9 | 0.311 | 0.360 | 2.682 | 0.209 | 0.359 | 0.732 | 0.641 | 0.241 | 15 | 1.5 |
| 10 | 0.377 | 0.215 | 2.853 | 0.126 | 0.568 | 0.686 | 0.432 | 0.372 | 20 | 1.3 |

^a Analysis carried out with program FITCO. TRIAD [2].

^b Analysis carried out with program MIXCO TRIAD [3].

^c MD = mean deviation between the observed and the calculated triads

It is clear that the values of $r_{E,\kappa}$ are not constant. Some fluctuation of the $r_{E,\kappa}$ values may be expected because of the noise in the data, but the trends indicate that both sets of $r_{E,\kappa}$ values decrease with increasing E feed. This result suggests that the polymer system contains more than two components.

Pairwise analysis using a three-state B/B/B model

In this analysis, the triad values for two samples are fitted simultaneously to a three-state **B/B/B** model. The procedure has been described earlier [4]; the computer program used is TRIADY. In this analysis, the NMR triad intensities of two samples are fed into the computer program simultaneously. The optimal values of $r_{p,\kappa}$ and w_κ are obtained. The same procedure is used for all consecutive pairs of data.

The trends in the data are then noted, and the analyses repeated to achieve consistency.

The results of the analysis are given in Table VII. In all cases good agreement is observed between the observed and the calculated triad values. The analysis suggests that the three-component model is quite capable of describing the copolymerization. The values of $\{r_{p,\kappa}\}$ and $\{w_\kappa\}$ then provide the model parameters. The reactivity ratios for propylene are:

$$\text{component 1 : } r_{p,1} = 0.003 - 0.036$$

$$\text{component 2 : } r_{p,2} = 0.12 - 0.15$$

$$\text{component 3 : } r_{p,3} = 0.57 - 0.76$$

Note that for all three components the catalytic sites favor ethylene insertion. In components 1 and 2, ethylene is much more reactive than propylene. In component 3, propylene is more competitive with ethylene (albeit still less reactive).

The component weight factor for component 1 increases steadily with increasing ethylene feed, whereas the component weights for components 2 and 3 decrease. As expected, some noise is present in the calculated component weights. The component weight factors are plotted as a function of ethylene feed in Figure 2. By extrapolating the curves to the values where feed ethylene is 0, we deduce that in homopolymerization of propylene, only

TABLE VII
Pairwise analysis of the triad data for *E/P* copolymers^a

| No. | $r_{P,1}$ | $r_{P,2}$ | $r_{P,3}$ | No. ^b | w_1 | w_2 | w_3 | MD |
|------|-----------|-----------|-----------|------------------|-------|-------|-------|------|
| 1+2 | 0.003 | 0.127 | 0.651 | 1 | 0.007 | 0.317 | 0.677 | 0.04 |
| | | | | 2 | 0.007 | 0.310 | 0.683 | |
| 2+3 | 0.002 | 0.122 | 0.611 | 2 | 0.002 | 0.303 | 0.696 | 0.17 |
| | | | | 3 | 0.015 | 0.268 | 0.718 | |
| 3+4 | 0.006 | 0.141 | 0.573 | 3 | 0.015 | 0.292 | 0.693 | 0.27 |
| | | | | 4 | 0.017 | 0.198 | 0.785 | |
| 4+5 | 0.010 | 0.129 | 0.635 | 4 | 0.021 | 0.210 | 0.770 | 0.27 |
| | | | | 5 | 0.143 | 0.062 | 0.795 | |
| 5+6 | 0.016 | 0.118 | 0.653 | 5 | 0.187 | 0.000 | 0.813 | 0.25 |
| | | | | 6 | 0.173 | 0.214 | 0.613 | |
| 6+7 | 0.019 | 0.119 | 0.610 | 6 | 0.194 | 0.166 | 0.641 | 0.25 |
| | | | | 7 | 0.156 | 0.202 | 0.642 | |
| 8+9 | 0.024 | 0.138 | 0.648 | 8 | 0.269 | 0.095 | 0.636 | 0.40 |
| | | | | 9 | 0.155 | 0.219 | 0.626 | |
| 9+10 | 0.036 | 0.153 | 0.762 | 9 | 0.179 | 0.256 | 0.564 | 0.39 |
| | | | | 10 | 0.447 | 0.145 | 0.408 | |

^a Analysis carried out using program TRIADY [4].

^b Numbers corresponding to the sample numbers used in pairwise analysis.

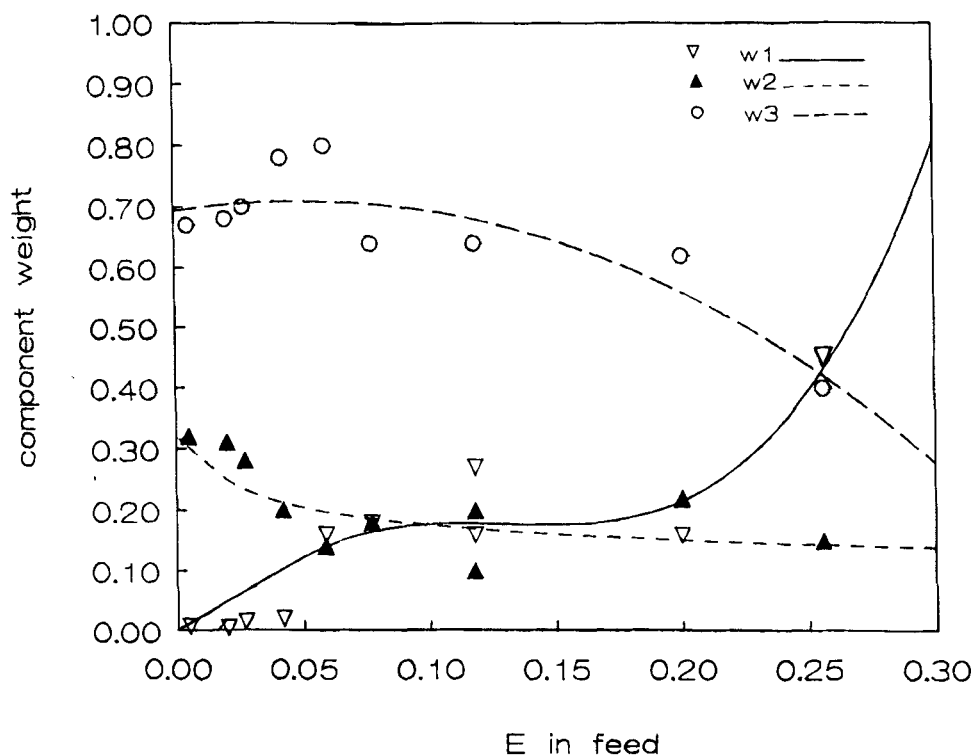


FIGURE 2 Component weight factors derived from pairwise analysis (∇ , \blacktriangle , \circ) and global fitting of all triads (—, ---, - - -) using three-state **B/B/B** model, plotted as a function of ethylene ratio in feed.

the catalytic sites corresponding to components 2 and 3 are active in the polymerization (component 2: 32%; component 3: 68%).

In the computer fitting, component 3 appears to be stable in all the iterations whereas components 1 and 2 show slight variations. The results in Table VII indicate that $\{r_{p,\kappa}\}$ are slightly dependent on the ethylene content. Thus, whereas the three-component model is acceptable for this analysis, the data can also be treated with a four-component model.

Global fitting of all triads

A further analysis can be carried out by taking all the triad data at once and fit them simultaneously to the three-state **B/B/B** model. One assumes that the component weights w_κ obey approximately polynomial expressions in the ethylene feed [$x = f_E/(f_E + f_P)$], within the range of polymer compositions studied.

$$w_2 = a_2 + b_2 x + c_2 x^2$$

$$w_3 = a_3 + b_3 x + c_3 x^2$$

$$w_1 = 1 - w_2 - w_3$$

The component weight factors and the propylene reactivities $r_{p,\kappa}$ of the three families of catalytic sites corresponding to the three polymeric components can be obtained through a nonlinear least-square fitting procedure [12]. The values of $\{r_{p,\kappa}\}$ that are consistent with the analysis of the previous section are given below:

$$\text{component 1 : } r_{p,1} = 0.003$$

$$\text{component 2 : } r_{p,2} = 0.120$$

$$\text{component 3 : } r_{p,3} = 0.852$$

The component weight factors are given by the following coefficients:

$$a_2 = 0.3037, \quad b_2 = 0.0704, \quad c_2 = -2.2155.$$

$$a_3 = 0.6968, \quad b_3 = -1.1944, \quad c_3 = -0.2286.$$

The calculated triad values for all ten samples in the global analysis are shown in Table VIII. The fit appears to be good for most of the samples. It is of interest to note that the two high ethylene samples (samples 9 and 10) show the largest deviations.

Note that if a set of data can be fitted to n -active sites, it can also be fitted to $(n + 1)$ active sites. In this case, the three-state **B/B/B** model is the simplest model that can fit the data. Equally good fit can be obtained using a four-component model. For the data available, however, a *unique* four-component model would be difficult to obtain. If a more fine-grained analysis is desired, we need additional analytical data. It has been shown earlier, for example, that supplementary data on molecular weight distribution [13], or fractionation [3,4] can uncover additional components.

CONCLUSION

In this work, a new solution process for E/P copolymerization, in which the monomer feed is kept constant throughout the polymerization, was used to prepare a series of E/P copolymers. Controlling the reaction in order to avoid inhomogeneities in the product-related to

TABLE VIII
 Observed^a and Calculated^b NMR triad data on E/P Copolymers

| No. | Feed E % | PPP | PPE | EPE | PEP | EEP | EEE |
|-----|-------------|------------------|------------------|----------------|-----------------|------------------|------------------|
| 1 | 0.5 | 94.28 (94.79) | 3.43 (3.14) | 0.20 (0.12) | 1.65 (1.57) | 0.31 (0.25) | 0.15 (0.13) |
| 2 | 2.0 | 81.16 (81.78) | 10.65 (9.56) | 0.83 (0.80) | 5.39 (4.78) | 1.44 (1.59) | 0.52 (1.50) |
| 3 | 2.7 | 77.27 (76.81) | 12.31 (11.59) | 1.27 (1.17) | 6.17 (5.80) | 2.05 (2.34) | 0.93 (2.29) |
| 4 | 4.2 | 71.59 (67.80) | 14.09 (14.67) | 1.57 (2.02) | 8.06 (7.33) | 3.20 (4.03) | 1.48 (4.15) |
| 5 | 5.9 | 61.94 (59.50) | 13.20 (16.80) | 3.06 (2.96) | 7.10 (8.40) | 5.26 (5.92) | 9.44 (6.42) |
| 6 | 7.7 | 47.13 (52.22) | 17.01 (18.14) | 4.86 (3.87) | 9.43 (9.07) | 9.82 (7.75) | 11.75 (8.95) |
| 7 | 11.8 | 37.42 (39.31) | 19.99 (19.29) | 6.29 (5.60) | 10.76 (9.65) | 11.62 (11.21) | 13.92 (14.94) |
| 8 | 11.8 | 37.39 (39.31) | 18.00 (19.29) | 6.46 (5.60) | 9.38 (9.65) | 10.95 (11.21) | 17.82 (14.94) |
| 9 | 20.0 | 25.52 (22.13) | 20.50 (17.95) | 8.28 (7.97) | 10.95 (8.97) | 15.79 (15.94) | 18.97 (27.03) |
| 10 | 25.6 | 14.06 (14.40) | 13.36 (15.61) | 9.18 (8.99) | 7.48 (7.80) | 16.61 (17.97) | 39.31 (35.23) |

^aObserved data calculated from Table IV.

^bCalculated data in parentheses are from global analysis achieved with program MINSQ/SCIENTIST [12].

all aspects other than the active site- allowed us to analyze the polymer in terms of a multicomponent polymer, the heterogeneous nature of which depends only on the catalyst and the associated presence of different types of active centers.

A computer-aided methodology was used for the analysis of ¹³C-NMR data and showed the E/P copolymers to contain at least three components. Thus, at least three families of catalytic sites exist in the catalyst used, two of which show an ethylene reactivity much higher than that of propylene. With the third type of sites, the reactivity of propylene approaches that of ethylene.

The presence of different families of active centers was expected as these kind of copolymers can be fractionated by solvents. The computer-assisted NMR analysis gives detailed information on the distribution of reactivities of the active centers, and requires much less work than a fractionation followed by NMR analysis. The catalyst comprises active centers which are much more reactive toward ethylene than toward propylene, as is generally observed in Ziegler-Natta catalysis. The presence of a third family of sites that is dominant at high propylene content, and that has a rather high propylene reactivity is in general unusual, but not surprising in this case as the catalyst used here was designed for propylene homopolymerization.

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