

Structural Analysis of Ethylene/Propylene Copolymer Synthesized Using High Activity Bi-supported Ziegler-Natta Catalyst

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ABSTRACT

Slurry copolymerization of ethylene and propylene (EPM) was carried out in dry n-heptane using high activity catalyst system of $\text{SiO}_2/\text{MgCl}_2/\text{TiCl}_4/\text{EB}/\text{TiBA}$ (or TEA)/MPT/ H_2 . The structure of four EPM samples with ethylene content of 30%, 40%, 50% and 80% were analyzed using ^{13}C NMR method. The complex spectra taking at high field are interpreted as resulting from ethylene propylene sequence placements. A methylene sequence distribution from one to six is given for four different ethylene propylene copolymer samples distribution. Increasing ethylene content of the copolymer increased EEE triad and decreased PPP triad distributions. Due to higher activity of ethylene monomer increasing its content from 30% to 80% the EEE triad distribution increased from 4.5% to about 73%. In the sample containing 30% of ethylene the PPP triad was less than 30% which is an indication of very high relative activity of ethylene to propylene for copolymerization using the catalyst system. The catalyst system used was quite active for the copolymerization and may introduce alternative sequence distribution in the polymer chain. Higher portion of propylene in the copolymer significantly increased the sequence of single methylene units and decreased six and more consecutive units. The EPM copolymer containing 30% to 50% ethylene have amorphous properties.

Key Words:

^{13}C NMR;
EPM;
structural analysis;
triad distribution;
Ziegler-Natta catalyst.

INTRODUCTION

Since the discovery of the Ziegler-Natta catalyst, these catalysts have been used for polymerization and copolymerization of α -olefins. Ethylene-propylene copolymers (EPM) such as impact EP strength modifier and EP elastomer are industrially

important materials. EPM Copolymer was traditionally carried out using homogeneous Ziegler-Natta catalyst based on vanadium compounds such as VC_3 or VOC_3 [1-3]. Also a number of titanium based catalyst systems have been used for the

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Table 1. Copolymerization conditions of ethylene-propylene and the results obtained using SiO₂/MgCl₂/TiCl₄/EB/TiBA (or TEA)/MPT catalyst system [9].

| Samples | Temp. (°C) | [Al]/[Ti] Molar ratio | P _p /P _E | Cocatalysts type | Yield (gEPM) | \bar{R}_p (gEPM/mmolTi.h) | Percentage of Et in copolymer (%) |
|---------|------------|--------------------------|--------------------------------|---------------------|-----------------|--------------------------------|--------------------------------------|
| 1 | 60 | 400 | 1.4 | TEA | 15.2 | 431.1 | 30 |
| 2 | 60 | 320 | 1.4 | TiBA | 36 | 1206.7 | 40 |
| 3 | 60 | 480 | 1.4 | TiBA | 23.8 | 793.6 | 50 |
| 4* | 55 | 320 | 1.4 | TiBA | 61.7 | 1722.3 | 80 |

[Ti] = 3.12×10^{-2} mmol; polymerization time = 1h; solvent = 400 mL heptane; TiBA = triisobutyl aluminium; TEA = triethyl aluminium; EB = ethylbenzoate; MPT = methyl-*p*-toluate. * $[H_2]$ = 150 mL/Lit solvent

copolymerization [2, 4, 5-7]. Polymers which are made through heterogeneous Ziegler-Natta catalysts often exhibit compositional heterogeneity. The behaviour is due to multiple catalytic sites present in the systems [8, 9]. Single site metallocene catalysts based on Zr and Ti activated with methylaluminoxane (MAO) was used for EPM production [10, 11].

The physical properties of EP random copolymer are strongly dependent upon the monomer distribution as well as on the number of chemically inverted propylene units (contain head-to-head and tail-to-tail structures for propylene) in the polymer chain [5, 8, 12-14]. ¹³C NMR Technique is one of the best effective method used for structural characterization of EPM [14-16]. We studied ethylene-propylene copolymerization behaviour carried out using heterogeneous Ti based Ziegler-Natta catalyst which have been reported [4, 9]. In the present work ¹³C NMR study was used for structural analysis of some of the samples of EPM were obtained. The methylene sequence distributions and methylene number average sequence lengths have been estimated.

EXPERIMENTAL

1,4-Dichlorobenzene (Merck) was used as solvent for EPM. Other chemicals, catalyst preparation method, polymerization procedure, and determination of ethylene content of EPM are explained elsewhere [9]. Et% was determined using an IR method (FTIR, Bruker model IFS48) preparing a film from polymer samples [9]. 75.4 MHz ¹³C NMR Spectra of EPM were obtained using Bruker AC 300 pulse NMR spectrometer with broad-band proton decoupling at 90°C. The sample solution was prepared in 1,4-dichlorobenzene.

Ethylene content of the copolymer was determined according to references 17 and 19.

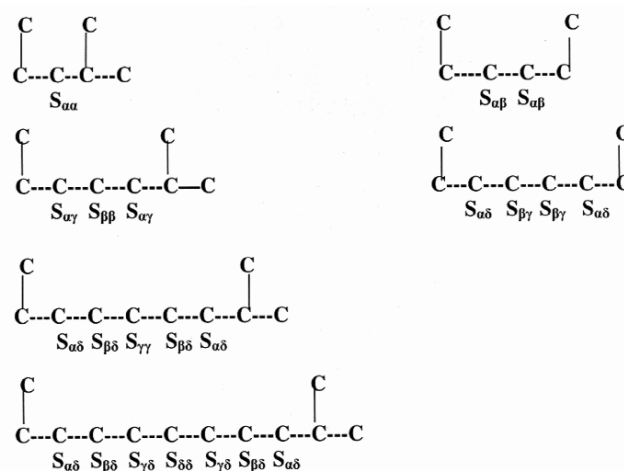
RESULTS AND DISCUSSION

Copolymerization

EPM Samples of known Et% content of 30, 40, 50, and 80% were chosen for the structural study. Table 1 shows the polymerization results obtained and the condition used for their preparations. Further details of the copolymerization are given in reference 9.

¹³C NMR Analysis

The assignments of all resonance peaks followed the terminology where primary (methyl), secondary (methylene), tertiary (methane) carbons were denoted as p, s, and t, respectively. The position of a carbon relative to its nearest methane groups was labeled by two Greek subscripts as shown in Figure 1 [16].

**Figure 1.** Nomenclature used for the methylene carbon of EPM.

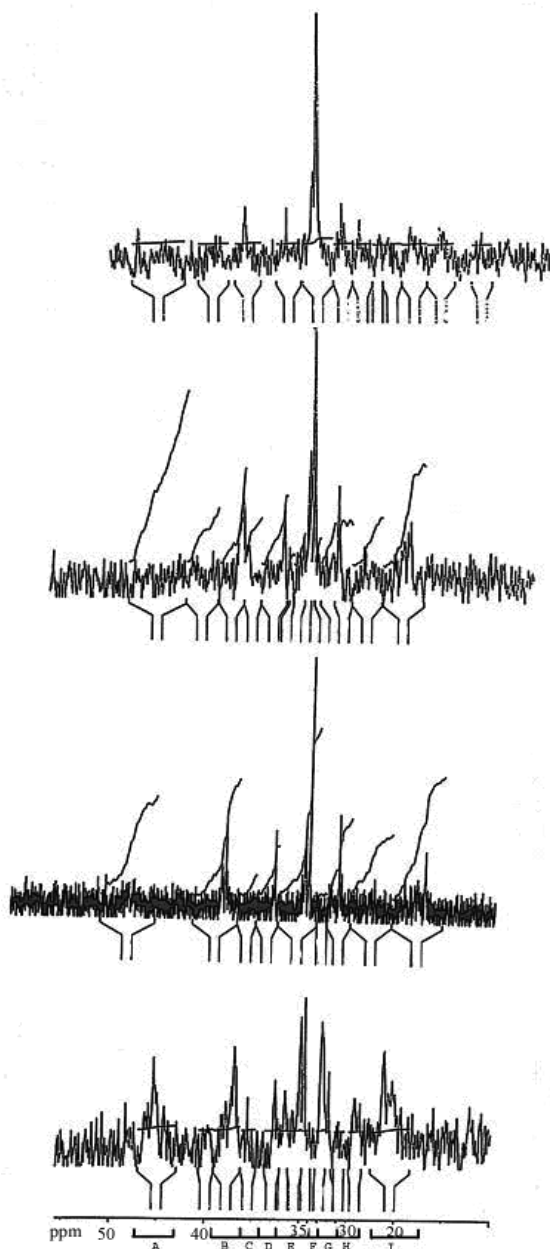


Figure 2. ^{13}C NMR Spectra of ethylene-propylene copolymer.

The ^{13}C NMR nomenclatures for the EPM copolymer samples contain 30, 40, 50 and 80% of ethylene are given in Figure 2. The detailed assignments and relative chemical shifts are presented in Table 2. The results are compared with other workers' results [15,16,18,19].

Comonomer Sequence Distribution

The assignments for each resonance and integral in the ^{13}C NMR spectra are shown in Table 2. The resonance

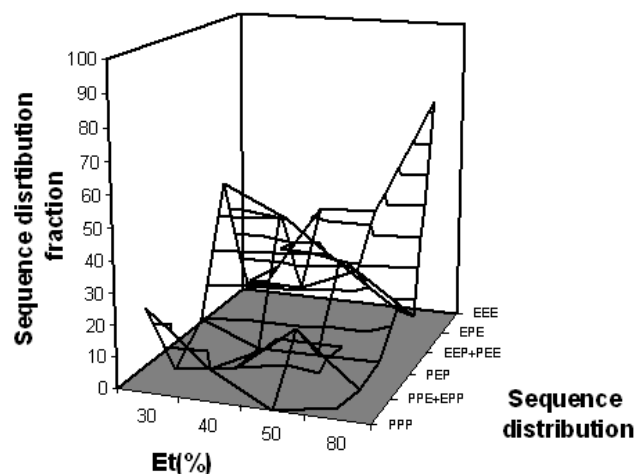


Figure 3. Comonomer sequence distribution in ethylene-propylene copolymers.

areas of methylene and methine average carbons were used for the calculations. The relationships between the triad distributions and the integrals are [14]:

$$\rho(\text{PPP}) = k(I_A - I_B + I_D + 5I_G + I_H) \quad (1)$$

$$\rho(\text{PPE+EPP}) = k(2I_B - 2I_D - I_G + I_H) \quad (2)$$

$$\rho(\text{EPE}) = k(I_D) \quad (3)$$

$$\rho(\text{EEE}) = 5k(I_E + I_F - I_A - I_B + I_D + I_H) \quad (4)$$

$$\rho(\text{PEP}) = k(I_H) \quad (5)$$

$$\rho(\text{PEE+EPP}) = k(I_G) \quad (6)$$

Where k is the NMR signal proportionality constant, I_S is the integral area with their subscripts denoting the integral ranges in Figure 1. The $\rho(\text{ijk})$ s are the triad ijk (E and P) distributions. As the propylene levels in the copolymers were low, area F did not much separate from area E. The triad distributions were calculated using eqns (1) to (6) and were presented in Table 3 and Figure 3. These values were found to be strongly dependent on the copolymer composition. Figure 3 shows increasing the ethylene content increased the triad distribution EEE and decreased PPP. The significant alternating triad distribution of (EPE), (PEP) and (EEP) were found.

Methylene Sequence Length

A unique carbon sequence cannot be described by a single succession of ethylene and propylene units such

Table 2. ^{13}C NMR Assignments and chemical shifts of methylene group of EPM [15, 16].

| Area | Integration | Chemical shift (ppm) | Carbon type | Our work |
|------|-------------|----------------------|---|---|
| A | 4305-48.5 | 48.1-45.3 | $S_{\alpha\alpha}$ | $S_{\alpha\alpha}$ |
| B | 36.1-39.8 | 38.8 | $S_{\alpha\gamma}$ | $S_{\alpha\gamma}$ $S_{\alpha\delta}$ |
| | | 38.4 | $S_{\alpha\delta}$ | |
| | | 37.9 | $S_{\alpha\gamma}$ | |
| | | 37.6 | $S_{\alpha\delta}$ | |
| C | 36.1-34.3 | 35.7 | $S_{\alpha\beta}$ | $S_{\alpha\beta}$ |
| | | 34.9 | $S_{\alpha\beta}$ | |
| D | 32.4-34.3 | 33.8 | $T_{\gamma\gamma}$ | $T_{\delta\delta}$ |
| | | 33.5 | $T_{\gamma\delta}$ | |
| | | 33.2 | $T_{\delta\delta}$ | |
| E | 32.4-29.1 | 31.2 | $T_{\beta\gamma}$ | $T_{\beta\gamma}$ |
| | | 30.9 | $T_{\beta\delta}$ | $T_{\beta\delta}$ |
| | | 30.85 | $S_{\gamma\gamma}$ | $S_{\gamma\gamma}$ |
| | | 30.8 | $T_{\beta\delta}$ | $T_{\beta\delta}$ |
| | | 30.4 | $S_{\gamma\delta}$ | $S_{\gamma\delta}$ |
| | | 28.7, 28.6 | $S_{\delta\delta}$ | $S_{\delta\delta}$ |
| F | 29.1-28.1 | 28.4 | $T_{\beta\beta}$ | |
| G | 28.1-25.8 | 27.8 | $S_{\beta\gamma}$ | $S_{\beta\gamma}$ |
| | | 27.45, 27.3 | $S_{\beta\delta}$ | $S_{\beta\delta}$ |
| H | 25.8-23.8 | 24.8, 24.7 | $S_{\beta\beta}$ | $S_{\beta\beta}$ |
| I | 22.5-18 | 22-21.3 | $P_{\beta\beta}$ | $P_{\beta\beta}$ |
| | | 21.3-20.6 | $P_{\beta\beta} + P_{\beta\delta} + P_{\beta\gamma}$ | $P_{\beta\beta} + P_{\beta\delta} + P_{\beta\gamma}$ |
| | | 20.6-19.5 | $P_{\beta\beta} + P_{\beta\gamma} + P_{\beta\delta} + P_{\gamma\gamma}$ | $P_{\beta\beta} + P_{\beta\gamma} + P_{\beta\delta} + P_{\gamma\gamma}$ |

as EEP, EPE, etc. We denote N_i as the moles of methylene sequence of length i , the $S_{\alpha\alpha}$, $S_{\alpha\beta}$, $S_{\alpha\delta}$, $S_{\gamma\gamma}$ are uniquely related to N_1 , N_2 , N_4 and N_5 , as $S_{\gamma\gamma}$ is overlaid with $T_{\beta\delta}$.

N_3 can be estimated from $S_{\beta\beta}$ with a possible check of $S_{\alpha\gamma}$ resonance. Therefore [15]:

$$N_1 = k I_1 \quad (7)$$

$$N_2 = k [1/2(I_6 + I_7)] \quad (8)$$

$$N_3 = k I_{20} \quad (9)$$

$$N_4 = k (1/2 I_{18}) \quad (10)$$

$$N_5 = k [1/2(I_{19} - I_{15})] \quad (11)$$

It is also possible to obtain the relationships between $S_{\alpha\delta}$, $S_{\beta\delta}$ and N_i as indicated by ref. 15. The total value ΣN_i can be estimated from [15]:

$$\Sigma N_i = k [I_1 + I_{20} + 1/2(I_6 + I_7 + I_{18} + I_{19})] \quad (12)$$

The number fraction of each sequence length $X_{n,I}$ is defined by :

$$X_{n,I} = N_i / \Sigma N_i \quad (13)$$

The total number of even fractions of methylene

Table 3. Comonomer sequence distribution in ethylene-propylene copolymers synthesized with bi-supported Ziegler-Natta catalyst.

| Samples | Et (%) | ρ(EEE) (%) | ρ(EPE) (%) | ρ(PEE+EEP) (%) | ρ(PEP) (%) | ρ(PPE+EPP) (%) | ρ(PPP) (%) |
|---------|--------|------------|------------|----------------|------------|----------------|------------|
| 1 | 30 | 4.5 | 9 | 50 | 9.8 | 0 | 26.6 |
| 2 | 40 | 33.2 | 10.3 | 41.2 | 2.5 | 2.5 | 10.3 |
| 3 | 50 | 33.8 | 18.3 | 27 | 2.6 | 18.3 | 0 |
| 4 | 80 | 73.7 | 4.5 | 13.5 | 3 | 1.5 | 3.8 |

Table 4. Number fractions of uninterrupted methylene sequence and average sequence lengths for ethylene propylene copolymers.

| Sample | Et (%) | X _{n,1} | X _{n,2} | X _{n,3} | X _{n,4} | X _{n,5} | X _{n,6+} | ΣX _{n,2i} | P _{EE} | \bar{n}_0 | \bar{n}_{2+} |
|--------|--------|------------------|------------------|------------------|------------------|------------------|-------------------|--------------------|-----------------|-------------|----------------|
| 1 | 30 | 0.508 | 0.024 | 0.196 | 0.098 | 0.123 | 0.051 | 0.287 | 0.625 | 3.21 | 5.00 |
| 2 | 40 | 0.375 | 0.063 | 0.188 | 0.063 | 0.125 | 0.125 | 0.250 | 0.666 | 4.88 | 7.00 |
| 3 | 50 | 0.285 | 0.143 | 0.285 | 0.095 | 0.143 | 0.050 | 0.330 | 0.500 | 4.85 | 6.39 |
| 4 | 80 | 0.143 | 0.072 | 0.286 | 0.072 | 0.143 | 0.285 | 0.210 | 0.500 | 6.00 | 7.22 |

sequence is:

$$\Sigma X_{n,2i} = \Sigma N_{2i} / \Sigma N_i = (N_2 + N_4 / (1 - P_{EE})) / \Sigma N_i \quad (14)$$

P_{EE} is defined as the chain propagation probability for ethylene inserted into an active centre with terminal monomer group of ethylene.

The number average sequence length of uninterrupted methylene carbons (\bar{n}_0 , note that \bar{n}_0 has the same meaning as \bar{n}_i here) and that of uninterrupted sequence of two or more methylene carbons (\bar{n}_{2+}) are [14]:

$$\bar{n}_0 = (I_1 + I_6 + I_7 + 3I_{20} + 2I_{18} + 2.5I_{19} + .5I_{15} + I_{16}) / (I_1 + I_{20} + .5(I_6 + I_7 + I_{18} + I_{19})) \quad (15)$$

$$\bar{n}_{2+} = (I_6 + I_7 + 3I_{20} + 2I_{18} + 2.5I_{19} + .5I_{15} + I_{16}) / (I_{20} + .5(I_6 + I_7 + I_{18} + I_{19})) \quad (16)$$

The calculated values of \bar{n}_0 , \bar{n}_{2+} , X_{n,1}, X_{n,2}, X_{n,3}, X_{n,4}, X_{n,5}, X_{n,6+}, X_{n,2i} are presented in Table 4. The \bar{n}_0 and \bar{n}_{2+} values were found to be strongly dependent on the copolymer composition. These values show that the X_{n,2} to X_{n,5} of the samples obtained using the titanium based catalyst were higher than the [C₅Me₄(SiMe₂N tBu)]TiMe₂(CGC) catalyst (constrained geometry catalyst). However, the results obtained using vanadium based homogeneous catalyst show similar to Ti based catalyst results (Table 5)[15]. The results indi-

cated that the CGC catalyst had more long runs of polyethylene and polypropylene than the titanium and vanadium based Ziegler-Natta catalysts, in other words the monomer units in the EPM prepared using titanium based catalyst produced has more alternating unit than the EPM obtained using the CGC catalyst.

Table 5. Comparison of uninterrupted methylene sequence obtained using the Ti, V based catalyst and CGC catalyst [15].

| Sample | X _{n,2} | X _{n,3} | X _{n,4} | X _{n,5} | X _{n,6+} |
|--------|------------------|------------------|------------------|------------------|-------------------|
| 1 | 0.024 | 0.196 | 0.098 | 0.123 | 0.051 |
| 2 | 0.063 | 0.188 | 0.063 | 0.125 | 0.125 |
| 3 | 0.143 | 0.285 | 0.095 | 0.143 | 0.050 |
| 4 | 0.072 | 0.286 | 0.072 | 0.143 | 0.285 |
| V1* | 0.130 | 0.200 | 0.060 | 0.110 | 0.240 |
| V2* | 0.060 | 0.220 | 0.070 | 0.090 | 0.250 |
| V3* | 0.140 | 0.230 | 0.080 | 0.120 | 0.240 |
| V4* | 0.150 | 0.210 | 0.070 | 0.110 | 0.220 |
| CGC1* | 0.052 | 0.145 | 0.020 | 0.085 | 0.351 |
| CGC2* | 0.061 | 0.150 | 0.021 | 0.068 | 0.318 |
| CGC3* | 0.062 | 0.154 | 0.020 | 0.069 | 0.301 |
| CGC4* | 0.091 | 0.146 | 0.019 | 0.066 | 0.083 |

(*) Results obtained from ref. 15.

CONCLUSION

From the results and calculations performed the following conclusion is obtained

-Due to higher ethylene activity increasing ethylene content from 30% to 80% is the EEE triad distribution is increased from 4.5% to 73%.

-Methylene units sequences increased by increasing propylene in feed (0.14 to 0.51).

-The propylene composition has not so much effect on three, four and five methylene sequences.

-Increasing the propylene composition decreases the six and more consecutive methyl units (0.28 to 0.05).

-The titanium based bi-supported catalyst used may introduce alternative sequence distribution in the polymer chain.

-Even at polymer sample containing 30% of ethylene the PPP triad is less than 30%. The result indicated a much lower relative reactivity of propylene to ethylene for copolymerizing onto the polymer chain or coordinating to catalytic active centre.

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