Structural Analysis of Ethylene/Propylene Copolymers Synthesized with a Constrained Geometry Catalyst

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ABSTRACT: The chain structures of five ethylene/propylene copolymer samples with propylene mole fractions of 0.277, 0.308, 0.321, 0.583, and 0.587 were analyzed and reported in this paper. These polymers were synthesized in a solution continuous stirred-tank reactor (CSTR) at 130−150 °C using a constrained geometry catalyst (CGC). The copolymers had polydispersities close to 2. Inverted propylene units were present. A large number of long runs of polyethylene and polypropylene units were also observed. Increasing the propylene composition significantly increased the sequences of one and two methylene units and decreased those of six and more consecutive methylene units. However, the uninterrupted methylene sequence distributions were little influenced by polymerization temperature. The meso and racemic contents in the continuous and inverted propylene units were approximately equal, indicating that the CGC did not have much control over the stereoregularity of the propylene insertion. Compared to the vanadium ethylene propylene elastomers (EPM), the CGC EP copolymers had fewer alternating comonomer sequences and more consecutive ethylene and propylene units.

Introduction

Ethylene (E)−propylene (P) copolymers are industrially important materials, such as EP elastomer (EPM, random and amorphous copolymer) and EP impact-strength modifier (block copolymer).[1,2] Extensive research has been carried out to relate the physical properties and performance with the chain structure of EP copolymers. Among different methods for the structural characterization, ^{13}C NMR has been found to be a most effective technique.[3−7]

The commercial EP copolymers are generally made using homogeneous aspecific vanadium-based and heterogeneous isospecific titanium-based Ziegler−Natta catalysts.[1,2] The advent of metallocene catalysts has offered a new route to synthesize EP copolymers with narrow molecular weight distributions and special stereochemical structures, providing both practical and fundamental interest. Recently, a half-sandwich complex called “constrained geometry catalyst” (CGC) has been developed which can form a long chain branched structure in olefin polymers, which have an excellent combination of mechanical properties and processability.[8] Its open geometry structure permits the active center to readily incorporate high α-olefins and ethylene macromonomers.[9] We have reported the kinetics of ethylene solution homopolymerization and copolymerization with octene-1 in a high-temperature, high-pressure continuous stirred-tank reactor (CSTR) using CGC systems.[10−12] The ethylene macromonomers were found to be generated mainly via chain transfer to ethylene, and the branched structures in the polyethylene were formed through an in situ copolymerization of the macromonomer with ethylene. The ethylene homopolymers and copolymers with octene-1 have narrow molecular weight distributions and narrow copolymer composition distributions.[10−13]

In this paper, we used our high-temperature CSTR system and synthesized ethylene/propylene copolymers with CGC. The chain structures for five EP copolymer samples produced at 130, 140, and 150 °C, respectively, were determined by ^{13}C NMR. The uninterrupted methylene sequence distributions, methylene number-average sequence lengths and tacticities for these copolymers were estimated. The comparison with six vanadium EPM samples was also presented in this paper.

Experimental Part

Polymer Preparation. EP copolymers were synthesized in the high-temperature high-pressure CSTR at 3.45×10^3 kPa with a mean residence time of 4 min. Three temperatures, 130 (sample 1), 140 (samples 2−4), and 150 °C (sample 5) were used. The CGC catalyst system included $[C_5Me_4(SiMe_2N^tBu)]$-$TiMe_2$ (Me, methyl; ^{t}Bu, isobutyl; C_5, cyclopentadiene) (CGC−Ti) and tris(pentafluorophenyl)boron (TPFPB), both provided by Dow Chemical, as 10 and 3 wt % solutions in Isopar E (an industrial solvent of saturated hydrocarbons from Van Waters & Rogers Ltd.), and modified methylaluminoxane (MMAO) supplied by Akzo-Nobel Corp. with 12 mol % of isobutyl replacement. Three components were mixed with a fixed molar ratio of 1:3:10 for all runs. Metal Ti concentration was controlled at 15 μM for samples 1−4 and 25 μM for sample 5. Isopar E was dried over a mixture of 4A and 13X molecular sieves from Aldrich and silica gel from Caledon Laboratories Ltd., and was deoxygenated by sparging with ultrahigh purity nitrogen (99.999%, Matheson Gas). Polymerization-grade ethylene and propylene from Matheson Gas were purified by CuO, Ascarite, CaH_2 and molecular sieves. Propylene was mixed with Isopar E to form a homogeneous solution in a comonomer tank before use. During polymerization, the comonomer tank was kept at a constant pressure of 180 psig balanced by pressurized nitrogen. The mole fractions of propylene in the polymerizing mixture were 0.529 (sample 1), 0.615 (sample 2), 0.655 (sample 3), 0.822 (sample 4), and 0.824 (sample 5). The polymerization procedure was referred to ethylene/octene-1 copolymerzation.[12] The details regarding the CSTR system setup were reported in our previous work.[10,12]

Polymer Characterization. The 75.4 MHz ^{13}C NMR spectra were obtained on a Bruker AC 300 pulsed NMR spectrometer with broad-band proton decoupling at 120 °C. The sample solutions were prepared in deuterated *o*-dichlorobenzene (*d*-ODCB) and 1,2,4-trichlorobenzene (TCB) at a concentration of around 35 wt % using 10 mm sample tubes.

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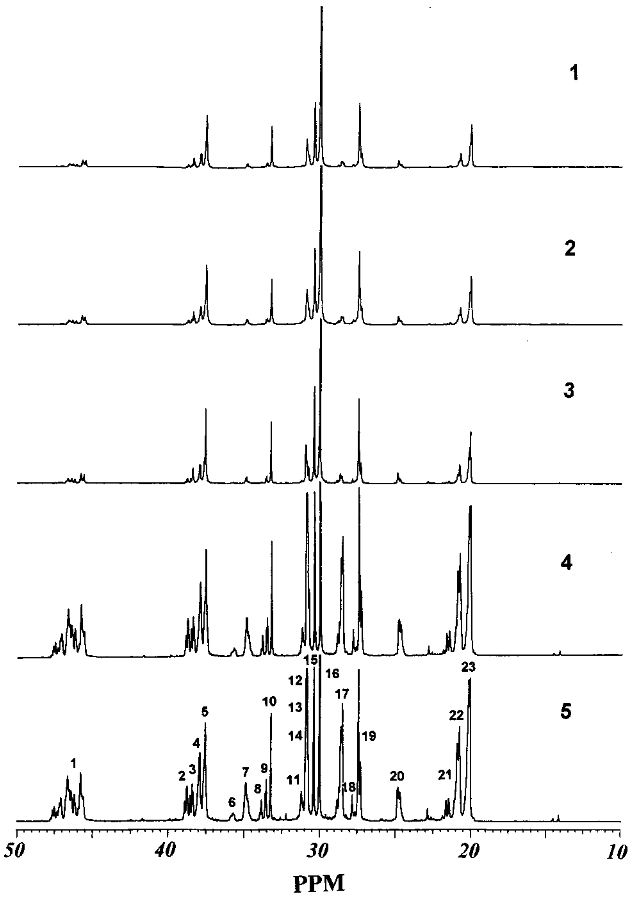

Figure 1. ^{13}C NMR spectra of CGC ethylene/propylene copolymers at 120 °C.

Table 1. ^{13}C NMR Assignment of Ethylene/Propylene Copolymer[a]

peak (no.)	carbon type	chemical shift (ppm)	integration limits (ppm)	area
1	$S_{\alpha\alpha}$	48.1−45.3	48.5−43.5	A
2	r-$S_{\alpha\gamma}$	38.8	39.8−36.1	B
3	r-$S_{\alpha\delta}$	38.4		
4	(m + other)-$S_{\alpha\gamma}$	37.9		
5	(m + other)-$S_{\alpha\delta}$	37.6		
6	r-$S_{\alpha\beta}$	35.7	36.1−34.3	C
7	(m + other)-$S_{\alpha\beta}$	34.9		
8	$T_{\gamma\gamma}$	33.8	34.3−32.4	D
9	$T_{\gamma\delta}$	33.5		
10	$T_{\delta\delta}$	33.2		
11	$T_{\beta\gamma}$	31.2	32.4−29.1	E
12	$T_{\beta\delta}$ (m)	30.9		
13	$S_{\gamma\gamma}$	30.85		
14	$T_{\beta\delta}$ (r)	30.8		
15	$S_{\gamma\delta}$	30.4		
16	$S_{\delta\delta}$	30.0		
17	$T_{\beta\beta}$	28.7, 28.6, 28.4	29.1−28.1	F
18	$S_{\beta\gamma}$	27.8	28.1−25.8	G
19	$S_{\beta\delta}$	27.45, 27.3		
20	$S_{\beta\beta}$	24.8, 24.7	25.8−23.8	H
21	$P_{\beta\beta}$(mm)	22.0−21.3	22.5−18.0	I
22	$P_{\beta\beta}$(mr) + $P_{\beta\gamma}$(m) + $P_{\beta\delta}$(m)	21.3−20.6		
23	$P_{\beta\beta}$(rr) + $P_{\beta\gamma}$(r) + $P_{\beta\delta}$(r) + $P_{\gamma\gamma}$	20.6−19.5		

[a] Referenced to isolated methylenes at 30.0 ppm.

Chemical shifts were referred to isolated methylenes at 30.0 ppm. As only methylene and methine resonance peaks were chosen for the calculations and the spin−lattice relaxation times of these carbons were less than 2 s, a delay time of 10 s between pulses was used.[10,14] At least 3000 scans were utilized to achieve a good signal-to-noise ratio.

Molecular weights and molecular weight distributions of the copolymers were measured by a Waters-Millipore 150 C high-temperature SEC in TCB at 140 °C using a differential refractive index detector. The universal calibration was performed against the known monodisperse TSK polystyrene standards from TOYO SODA Mfg.

Results and Discussion

Copolymer Composition. The ^{13}C NMR spectra for the five EP copolymer samples are given in Figure 1. The assignments of all resonance peaks followed the terminology used by Carman et al.[3] and Cheng,[7] where primary (methyl), secondary (methylene) and tertiary (methine) carbons were denoted as P, S, and T, respectively. The position of a carbon relative to its nearest methine groups was labeled by two Greek subscripts. The detailed assignments are shown in Table 1. For a clear indication of the configurations, a nomenclature was utilized with "1" referring to methine/methyl carbons and "0" to methylene carbons in defining head/tail structure and with "m" referring to meso and "r" to racemic in defining tacticity.[7]

Different EP copolymers were synthesized by metallocene catalysts. No significant head-to-head and tail-to-tail structures (inverted propylene sequences) were reported in the metallocene EP copolymers, even when aspecific metallocenes were used.[15] However, EPM synthesized with vanadium-based catalysts contained a large number of propylene inverted units as well as meso and racemic pairs.[4,7] In the presence of propylene inversion and tacticity, the vanadium EPM can be viewed as a five-component copolymer of ethylene, m-propylene, r-propylene, inverted m-propylene, and inverted r-propylene, respectively. The inverted structure of 1001 (head-to-head) can be observed from resonances of $S_{\alpha\beta}$, $T_{\gamma\gamma}$, $T_{\gamma\delta}$, and $T_{\beta\gamma}$, while 100001 can be observed from $S_{\beta\gamma}$. From the ^{13}C NMR spectra as shown in Figure 1, considerable 1001 and 100001 chain structures were identified in the CGC EP copolymers, indicating that the monomer units in the copolymer chains were randomly distributed and the copolymers did not follow a regular alternating sequence of ethylene and propylene units. The spectra showed the resonances similar to those of the vanadium EPM samples.[4,7] No 0110 structure (tail-to-tail inversion at a $T_{\alpha\beta}$ chemical shift of 40.8 ppm) was detected in the five samples. The formation of 1001 structure depended on the terminal propylene arrangement in the propagating center (A). If the center was a 01A type, an ethylene insertion followed by a propylene addition in the inverted direction (10) formed the 1001 structure. Another possibility was to insert the propylene unit into a 10A type center in the 01 arrangement. It is very difficult to clarify which reaction was dominant in the 1001 formation. These reaction pathways also applied to the formation of the 100001 structure.

Table 2 gives the molecular weight distributions for the five copolymer samples. The molecular weight distributions close to 2 indicated that the CGC catalyst system synthesized narrow MW distributed EP copolymers.

Propylene compositions in the copolymers can be estimated using the calculation scheme proposed by

Table 2. Propylene Mole Fractions and Molecular Weights for Ethylene/Propylene Copolymers

sample	T (°C)	F_P	M_w ($\times 10^{-4}$)	M_w/M_n
1	130	0.277	3.49	2.0
2	140	0.308	2.36	2.5
3	140	0.321	1.55	2.5
4	140	0.583	0.97	2.5
5	150	0.587	0.57	2.5
R1[4]		0.37		
R2[4]		0.38		
R3[4]		0.38		
R4[4]		0.41		
R5[4]		0.50		
R6[7] [a]		0.63		

[a] Calculated from the integrated spectral areas in ref 7.

Cheng.[7] Only total methylene (S) and methine (T) carbons were utilized for these calculations. The following relationships exist between the methylene and methine carbons:

$$S_{\alpha\alpha} = T_{\beta\beta} + {}^1/_2(T_{\beta\gamma} + T_{\beta\delta}) \tag{1}$$

$$S_{\alpha\beta} = T_{\beta\gamma} + T_{\gamma\delta} + 2T_{\gamma\gamma} \tag{2}$$

$$S_{\alpha\gamma} + S_{\alpha\delta} = T_{\beta\delta} + T_{\gamma\delta} + 2T_{\delta\delta} \tag{3}$$

Owing to the overlap of $S_{\gamma\gamma}$ and $T_{\beta\delta}$, the intensities of the two peaks can be separated using the following expression:[7,16]

$$S_{\gamma\gamma} = {}^1/_2(S_{\beta\delta} - S_{\gamma\delta}) \tag{4}$$

Therefore, the moles of propylene (p) and ethylene (e) units can be estimated from the following equations:

$$p_S = k[S_{\alpha\alpha} + {}^1/_2(S_{\alpha\beta} + S_{\alpha\gamma} + S_{\alpha\delta})]$$

$$p_T = k[T_{\gamma\gamma} + T_{\gamma\delta} + T_{\delta\delta} + T_{\beta\beta} + T_{\beta\gamma} + T_{\beta\delta}]$$

$$p = {}^1/_2(p_S + p_T) \tag{5}$$

$$e = k\{{}^1/_2[S_{\beta\beta} + S_{\beta\gamma} + S_{\beta\delta} + S_{\gamma\gamma} + S_{\gamma\delta} + S_{\delta\delta} + {}^1/_2(S_{\alpha\beta} + S_{\alpha\gamma} + S_{\alpha\delta})]\} \tag{6}$$

where k is the NMR signal proportionality constant. The quantity of propylene is based on the average of both methylene (p_S) and methine (p_T) carbon contributions.

Inserting eqs 1–4 into eqs 5 and 6 and utilizing the integral areas in Table 1 yield

$$p_S = k[I_A + {}^1/_2(I_B + I_C)]$$

$$p_T = k[2I_A + I_D - I_F] \tag{7}$$

$$e = k[{}^1/_2(I_D + I_E + I_F + I_G + I_H - I_A)] \tag{8}$$

where I's are the integral areas with their subscripts denoting the integral ranges in Table 1. The propylene mole fraction (F_P) in the copolymer is then

$$F_P = \frac{p}{p + e} \tag{9}$$

From eqs 7–9, the propylene mole fractions for the five copolymers were estimated and presented in Table 2. Samples 1, 2, and 3 had F_P about 0.3 and samples 4 and 5 about 0.6. For comparison purposes, six vanadium EPM samples[4,7] (samples R1–R6) were also included in Table 2.

Methylene Sequence Lengths. The ^{13}C NMR spectra clearly showed a high content of the inverted propylene sequences, which made the structural analysis difficult. A unique carbon sequence cannot be described by a single succession of ethylene and propylene units such as EPP, PEP, etc. An approach using methylene sequence distributions from one to six and longer consecutive methylene carbons was proposed to quantitatively study the sequence distributions.[3,4,17] We denote N_i as the moles of methylene sequences of length i. The $S_{\alpha\alpha}$ (peak 1), $S_{\alpha\beta}$ (peaks 6 and 7), $S_{\beta\gamma}$ (peak 18), and $S_{\gamma\gamma}$ (peak 13) are uniquely related to N_1, N_2, N_4, and N_5. As $S_{\gamma\gamma}$ is overlaid with $T_{\beta\delta}$, the former can be calculated by eq 4. N_3 can be estimated from $S_{\beta\beta}$ (peak 20) with a possible check of $S_{\alpha\gamma}$ (peaks 2 and 4) resonance. Therefore

$$N_1 = kS_{\alpha\alpha} = kI_1 \tag{10}$$

$$N_2 = k({}^1/_2S_{\alpha\beta}) = k[{}^1/_2(I_6 + I_7)] \tag{11}$$

$$N_3 = kS_{\beta\beta} = kI_{20} = k({}^1/_2S_{\alpha\gamma}) = k[{}^1/_2(I_2 + I_4)] \tag{12}$$

$$N_4 = k({}^1/_2S_{\beta\gamma}) = k({}^1/_2I_{18}) \tag{13}$$

$$N_5 = k(S_{\gamma\gamma}) = k[{}^1/_2(S_{\beta\delta} - S_{\gamma\delta})] = k[{}^1/_2(I_{19} - I_{15})] \tag{14}$$

From the ^{13}C NMR spectra, one can also obtain the relationships between $S_{\alpha\delta}$, $S_{\beta\delta}$, and $S_{\gamma\delta}$ and N_i.

$$\sum_{i=1}^{n} N_i - N_1 - N_2 - N_3 = k({}^1/_2S_{\alpha\delta}) = k[{}^1/_2(I_3 + I_5)] \tag{15}$$

$$\sum_{i=1}^{n} N_i - N_1 - N_2 - N_3 - N_4 = k({}^1/_2S_{\beta\delta}) = k[{}^1/_2I_{19}] \tag{16}$$

$$\sum_{i=1}^{n} N_i - N_1 - N_2 - N_3 - N_4 - N_5 = k({}^1/_2S_{\gamma\delta}) = k[{}^1/_2I_{15}] \tag{17}$$

The total value $\sum_{i=1}^{n} N_i$ can be estimated from

$$\sum_{i=1}^{n} N_i = k[S_{\alpha\alpha} + S_{\beta\beta} + {}^1/_2(S_{\alpha\beta} + S_{\beta\gamma} + S_{\beta\delta})] = k[I_1 + I_{20} + {}^1/_2(I_6 + I_7 + I_{18} + I_{19})] \tag{18}$$

with a check of

$$\sum_{i=1}^{n} N_i = k[S_{\alpha\alpha} + S_{\beta\beta} + {}^1/_2(S_{\alpha\beta} + S_{\alpha\delta})] \tag{19}$$

The number fractions of each sequence length ($x_{n,i}$) are defined by

$$x_{n,i} = N_i / \sum_{i=1}^{n} N_i \tag{20}$$

Table 3. Number Fractions of Uninterrupted Methylene Sequence and Average Sequence Lengths for Ethylene/Propylene Copolymers

sample	$x_{n,1}$	$x_{n,2}$	$x_{n,3}$	$x_{n,4}$	$x_{n,5}$	$x_{n,6+}$	$\sum_{i=1}^{n} x_{n,2i}$	P_{EE}	$\bar{n}_0$	$\bar{n}_{2+}$
1	0.347	0.052	0.145	0.020	0.085	0.351	0.125	0.581	5.90	8.50
2	0.382	0.061	0.150	0.021	0.068	0.318	0.133	0.453	5.22	7.82
3	0.394	0.062	0.154	0.020	0.069	0.301	0.128	0.451	4.93	7.49
4	0.595	0.091	0.146	0.019	0.066	0.083	0.127	0.450	2.37	4.39
5	0.597	0.098	0.141	0.018	0.061	0.084	0.133	0.433	2.35	4.36
R1[4]	0.26	0.13	0.20	0.06	0.11	0.24	0.27	0.55	4.4	5.6
R2[4]	0.31	0.06	0.22	0.07	0.09	0.25	0.20	0.41	4.5	6.1
R3[4]	0.19	0.14	0.23	0.08	0.12	0.24	0.31	0.52	4.3	5.4
R4[4]	0.24	0.15	0.21	0.07	0.11	0.22	0.30	0.52	4.2	5.2
R5[4]	0.30	0.17	0.20	0.08	0.09	0.17	0.32	0.45	3.5	4.6
R6[7] [a]	0.45	0.23	0.18	0.05	0.05	0.05	0.29	0.27	2.3	3.3

[a] Calculated from the integrated spectral areas in ref 7.

The copolymerization of ethylene with octene-1 using the CGC as catalyst was found to follow a first-order Markovian model.[12] The kinetic study of the ethylene and propylene copolymerization with the CGC also showed first-order Markovian copolymerization behavior.[18] From the uninterrupted methylene sequences, one can calculate the chain propagation probability for ethylene inserted into an active center with terminal monomer group of ethylene (P_{EE}):[17]

$$P_{EE} = N_5/N_3 \tag{21}$$

The total number fraction of even methylene sequences is[16]

$$\sum_{i=1}^{n} x_{n,2i} = \frac{\sum_{i=1}^{n} N_{2i}}{\sum_{i=1}^{n} N_i} = \frac{N_2 + \dfrac{N_4}{1 - P_{EE}}}{\sum_{i=1}^{5} N_5 + \dfrac{P_{EE}}{1 - P_{EE}}(N_4 + N_5)} \tag{22}$$

The number fractions of uninterrupted methylene sequences for the five CGC EP copolymers and six vanadium EPM samples are presented in Table 3. The CGC EP data demonstrated that the copolymer composition had a significant influence on the sequence distribution (compare samples 1–3 to samples 4 and 5) and that the effect of polymerization temperature was minor (compare sample 1 to samples 2 and 3; also compare sample 4 to sample 5). It was also observed that the $x_{n,2}$ to $x_{n,5}$ values of samples R1–R6 were higher than those of samples 1–5 (equivalently, that the $x_{n,1}$ and $x_{n,6+}$ values of the former were lower than the latter). These results indicated that the CGC EP copolymers had more long runs of polyethylene and polypropylene than the vanadium EPM samples. In other words, the monomer units in the vanadium EPM samples were more alternating than in the CGC EP copolymers. The lower $x_{n,2}$ and $x_{n,4}$ values in samples 1–5 compared to samples R1–R6 showed that the inversions in the CGC EP copolymers were lower than those in the vanadium EPM samples. The total number fractions of even uninterrupted methylene sequences for all five CGC copolymers were about 13%, lower than about 30% in samples R1–R6.

In the presence of propylene inverted insertion, it is only possible to determine the number-average sequence lengths of uninterrupted methylene carbons given by

$$\bar{n}_i = \sum_{j=i}^{n} jN_j / \sum_{j=i}^{n} N_j \tag{23}$$

but not the number-average sequence lengths of ethylene additions. For more than five carbons, the following relationship should hold:

$$\sum_{j=6}^{n} jN_j = k(3\mathrm{S}_{\gamma\delta} + \mathrm{S}_{\delta\delta}) = k(3I_{15} + I_{16}) \tag{24}$$

The number-average sequence length of uninterrupted methylene carbons ($\bar{n}_0$; note that $\bar{n}_0$ has the same meaning as $\bar{n}_1$ here) and that of uninterrupted sequences of two or more methylene carbons ($\bar{n}_{2+}$) are

$$\begin{aligned}\bar{n}_0 &= \frac{\mathrm{S}_{\alpha\alpha} + \mathrm{S}_{\alpha\beta} + 3\mathrm{S}_{\beta\beta} + 2\mathrm{S}_{\beta\gamma} + {}^5\!/_2\mathrm{S}_{\beta\delta} + {}^1\!/_2\mathrm{S}_{\gamma\delta} + \mathrm{S}_{\delta\delta}}{\mathrm{S}_{\alpha\alpha} + \mathrm{S}_{\beta\beta} + {}^1\!/_2(\mathrm{S}_{\alpha\beta} + \mathrm{S}_{\beta\gamma} + \mathrm{S}_{\beta\delta})} \\ &= \frac{I_1 + I_6 + I_7 + 3I_{20} + 2I_{18} + {}^5\!/_2 I_{19} + {}^1\!/_2 I_{15} + I_{16}}{I_1 + I_{20} + {}^1\!/_2(I_6 + I_7 + I_{18} + I_{19})}\end{aligned} \tag{25}$$

and

$$\begin{aligned}\bar{n}_{2+} &= \frac{\mathrm{S}_{\alpha\beta} + 3\mathrm{S}_{\beta\beta} + 2\mathrm{S}_{\beta\gamma} + {}^5\!/_2\mathrm{S}_{\beta\delta} + {}^1\!/_2\mathrm{S}_{\gamma\delta} + \mathrm{S}_{\delta\delta}}{\mathrm{S}_{\beta\beta} + {}^1\!/_2(\mathrm{S}_{\alpha\beta} + \mathrm{S}_{\beta\gamma} + \mathrm{S}_{\beta\delta})} \\ &= \frac{I_6 + I_7 + 3I_{20} + 2I_{18} + {}^5\!/_2 I_{19} + {}^1\!/_2 I_{15} + I_{16}}{I_{20} + {}^1\!/_2(I_6 + I_7 + I_{18} + I_{19})}\end{aligned} \tag{26}$$

The calculated values of $\bar{n}_0$ and $\bar{n}_{2+}$ are presented in Table 3. The $\bar{n}_0$ and $\bar{n}_{2+}$ values were found to be strongly dependent on the copolymer composition, with lower values at high propylene incorporation. The $\bar{n}_0$ and $\bar{n}_{2+}$ for the six EPM samples are also shown in Table 3 for comparison.

Tacticity. High contents of head-to-tail propylene units were found in the CGC EP copolymers (i.e., high $x_{n,1}$ values of samples 1–5 in Table 3). These copolymers were also similar to the vanadium EPM, having both syndiotactic and isotactic polypropylene structures.[7] The tacticities in these copolymers were evident from the fine structures of the ^{13}C NMR spectra. The configurations affecting the $\mathrm{S}_{\alpha\gamma}$ and $\mathrm{S}_{\alpha\delta}$ carbons are the continuous head-to-tail propylene units (m_1:r_1, m_1':r_1' and m_1'':r_1'') and the inverted propylene units (m_2:r_2) (see Table 4). Note that the subscripts “1” and “2” denote the

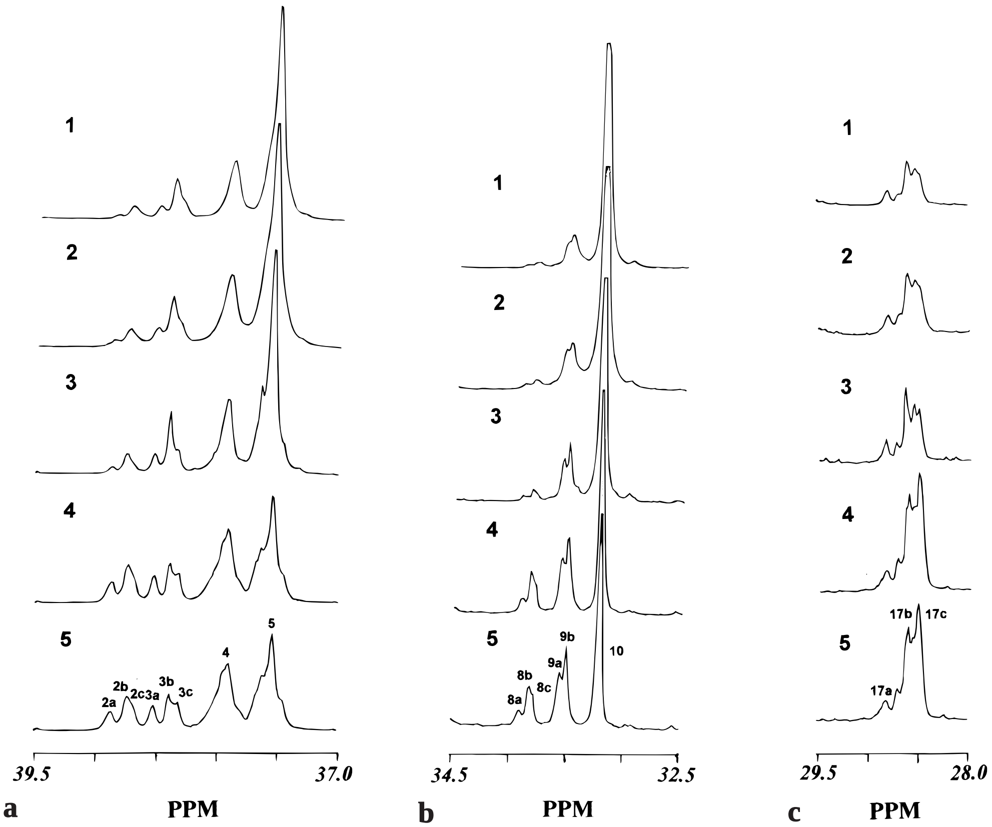

Figure 2. Expanded plot of ^{13}C NMR spectra; (a) from 39.5 to 37.0 ppm; (b) from 34.5 to 32.5 ppm; (c) from 29.5 to 28.0 ppm.

Table 4. Tacticity of Continuous and Inverted Propylene Units in Ethylene/Propylene Copolymers

sample	m_1:r_1 1010101010 └┘	m_1':r_1' 10101010100 └┘	m_1'':r_1'' 10101010100 └┘	m_1:r_1	m_2:r_2 01001 └─┘
1	0.47	0.51	0.49	0.49	0.52
2	0.48	0.49	0.45	0.47	0.52
3	0.47	0.49	0.45	0.47	0.51
4	0.41	0.47	0.45	0.44	0.50
5	0.42	0.45	0.45	0.44	0.48
R6[7]	0.37	0.35	0.34	0.35	0.55

number of continuous methylene units and the symbol "m:r" means m/(m + r). The expanded plots for these resonance regions are given in Figure 2a–c. The overlays between some peaks were resolved by the curve analysis.

The m_1:r_1 value was obtained from $T_{\beta\beta}$ (peak 17). Peak 17a and peaks 17b–c were assigned to (m_1m_1) and an ($m_1r_1 + r_1r_1$) triad, respectively. In general, the determination of tacticity requires the use of a Markovian reaction probability model. However, we did not have adequate information (m_1r_1 and r_1r_1 signals were overlapped) to apply a Markovian model to estimate the diad fractions. The Bernoullian model, $m_1^2 = m_1m_1$, was therefore selected to calculate the approximate probabilities. The m_1':r_1' value was estimated from the m_1'- and r_1'-$S_{\alpha\gamma}$, m_1'- and r_1'-$S_{\alpha\delta}$, and m_1'- and r_1'-$S_{\alpha\beta}$ carbons. As the resonance peaks of m_1'-$S_{\alpha\gamma}$ (peak 4), m_1'-$S_{\alpha\delta}$ (peak 5), and m_1'-$S_{\alpha\beta}$ (peak 7) were overlaid by other sequence structures, only the structure of 101010*0 in each peak (peaks 4, 5, and 7) was used for the calculation of m_1':r_1'. The m_1' values of this 101010*0 structure were calculated by the following relationships:

$$(m_1' - S_{\alpha\gamma}) + (r_1' - S_{\alpha\gamma}) + (m_1' - S_{\alpha\delta}) + (r_1' - S_{\alpha\delta}) = T_{\beta\delta} \quad (27)$$

$$(m_1' - S_{\alpha\beta}) + (r_1' - S_{\alpha\beta}) = T_{\beta\gamma} \quad (28)$$

The average of m_1'-$S_{\alpha\gamma}$, m_1'-$S_{\alpha\delta}$ and m_1'-$S_{\alpha\beta}$ and that of their corresponding r_1' values gave the ratio of m_1':r_1'. The resonances $m_1''r_1'$-$S_{\alpha\gamma}$, $r_1''r_1'$-$S_{\alpha\gamma}$, $m_1''r_1'$-$S_{\alpha\delta}$, and $r_1''r_1'$-$S_{\alpha\delta}$ correspond to peaks 2a, 2b, 3a, and 3b, respectively. The m_1'':r_1'' was estimated from the ratio of $I_{2a} + I_{3a}$ over $I_{2b} + I_{3b}$. Taking the average of the m_2 value using the Bernoullian model ($m_2^2 = I_{8a}/I_8$, peaks 8a, 8b, and 8c were assigned to m_2m_2-, m_2r_2-, and r_2r_2-$T_{\gamma\gamma}$, respectively) and that of I_{9a}/I_9 (peaks 9a and 9b were assigned to m_2- and r_2-$T_{\gamma\delta}$, respectively) gave m_2:r_2.

The tacticity results for the five CGC EP samples and one vanadium EPM sample[7] are given in Table 4. It is of interest to see that the values of the three m_1:r_1, m_1':r_1', and m_1'':r_1'' configurations in the five CGC samples were close to 50% meso configuration rather than 35% in the vanadium sample. In addition, the m_2:r_2 values were also close to 50% for different samples, which was close to that of the vanadium EPM sample. The polymerization temperature was observed to have little influence on the tacticity in the copolymers. In view of the steric control mechanism, the isotactic stereoregularity (high meso configuration) was found to be controlled by the asymmetry of the catalytic complexes while the syndiotactic stereoregularity (high racemic configuration) was determined by the asymmetry of the last unit in the growing chain.[19] The chiral catalytic site and the asymmetric monomer insertion were found to have compensative effects on the chain configuration for an aspecific catalyst.[19] The approximate 50% meso contents for both 101 and 1001 structures in the CGC EP copolymers indicated that the effects of the two factors canceled out. The CGC did not control the copolymer stereoregularity.

Conclusions

Five EP copolymer samples were synthesized with the CGC at 130, 140, and 150 °C and characterized using a ^{13}C NMR technique. Inverted propylene units were present in the copolymers. A high number of consecutive ethylene and propylene units were also observed. The copolymers had narrow molecular weight distributions with polydispersities close to 2. More sequences of one and two methylene units and less sequences of six and more consecutive methylene units were found with higher propylene composition, while the three, four, and five methylene sequences remained unchanged. The effect of polymerization temperature on the sequence distributions was minor. In comparison with the vanadium EPM samples, the CGC EP copolymers had fewer alternating monomer units and more consecutive ethylene and propylene units, indicating a higher block tendency of the CGC. The total number fractions of the even uninterrupted methylene sequences (indicating the inversion structures) in the CGC EP copolymers were about 13%, lower than about 30% in the vanadium EPM samples. The CGC EP copolymers had equal meso and racemic contents. Little stereoregularity control was observed with the CGC system.

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