

COMONOMER SEQUENCE DISTRIBUTION IN METALLOCENE-BASED ETHYLENE/1-BUTENE (S-34) AND ETHYLENE/1-HEXENE (S-43) COPOLYMERS

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Abstract Metallocene based polyethylenes were prepared by SINOPEC's "metallocene adduct" technology in a gas phase fluidized bed model reactor. The ^{13}C -NMR spectra of ethylene/1-butene (S-34) and ethylene/1-hexene(S-43) copolymers were studied in a manner analogous to that established by Hsieh and Cheng. The comonomer sequence distributions of copolymer samples were obtained. The results show that these metallocene based copolymers contain a small amount of butene and hexene, and the EE and EEE sequences are dominant.

Keywords Metallocene, Comonomer sequence distribution, ^{13}C -NMR

INTRODUCTION

Ethylene/1-butene (EB) and ethylene/1-hexene (EH) have attracted increasing attention because 1-butene and 1-hexene are used in ethylene polymerization to provide linear low density polyethylene. The microstructure of these two kinds of polymer have been studied by ^{13}C -NMR^[1-4]. Hsieh et al.^[1, 2] presented a ^{13}C -NMR method for a quantitative determination of the comonomer distribution, the triad and tetrad sequence distribution, average sequence lengths, and run numbers in ethylene/1-butene copolymers. Cheng^[4] has improved the ^{13}C -NMR assignments of EH copolymers and developed a computerized analytical methodology to obtain accurate comonomer sequence distribution.

In this work, S-34 and S-43 copolymers were prepared using metallocene catalyst in a gas phase fluidized bed model reactor. The ^{13}C -NMR spectra of EB and EH copolymers were analyzed in a manner analogous to that established by Hsieh and Cheng.

EXPERIMENTAL

Samples

S-34, S-43 was prepared by using supported metallocene 'adduct' as a catalyst in gas phase fluidized bed model reactor (CN98101789.4).

^{13}C -NMR Measurement

The samples were dissolved in o-dichlorobenzene- d_4 to give approximately 15% (W/V) solutions.

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Received November 11, 1997

The ^{13}C -NMR spectra were obtained on a Bruker DRX-400 spectrometer operating at 100.6 MHz and 383 K. The spectral width, acquisition time and data points were 10776 Hz, 0.76s and 16K, respectively. ^1H band-band decoupling and digital quadrature detection were used to remove ^{13}C (^1H) couplings. A 70° RF pulses ($8\ \mu\text{s}$) was used with a 20 s relaxation delay between pulses. The number of scans for each spectrum was about 2600 and a line broadening of 2 Hz was used to get satisfactory S/N ratio and separation among peaks. The intensity measurement was made by using an integration software of the spectrometer.

RESULTS

Ethylene/1-Butene Copolymer (S-34)

The ^{13}C -NMR spectrum of S-34 is shown in Fig. 1.

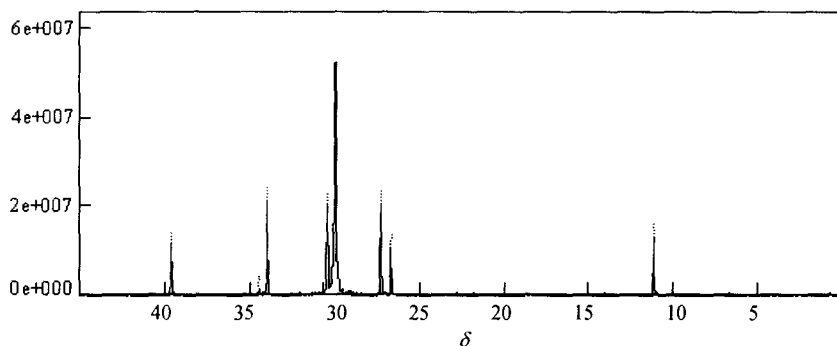
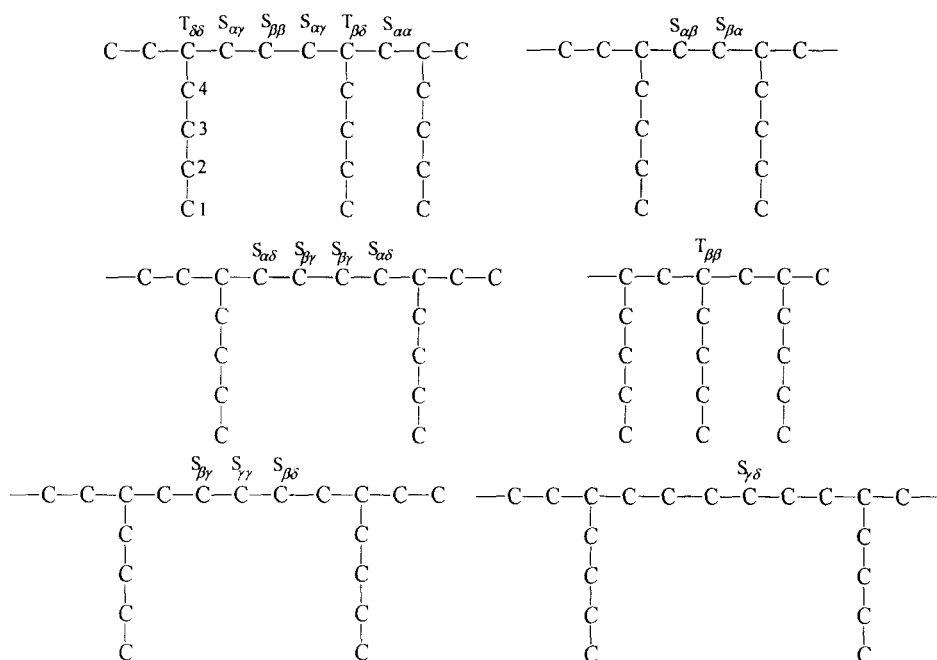
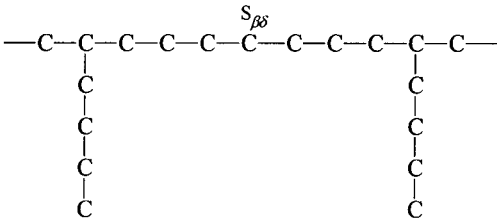


Fig. 1 ^{13}C -NMR spectrum of S-34 in $\text{C}_6\text{H}_4\text{Cl}_2\text{-}d_4$ ($T = 383\text{K}$)

The spectral lines were numbered as 1-24 according to the results of Hsieh et al. The assignment of ^{13}C spectral lines of S-34 were made by comparing the chemical shifts calculated through additivity relationships and reference polymers^[1, 2]. According to the idea of Carman^[5] the nomenclature of EH polymer are as follows:





The nomenclature of EB copolymer is similar to that of EH copolymer. There are butyl branches in EH copolymer, but with only ethylene branches in EB copolymer. In the nomenclature of EH and EB, S and T represent the secondary and tertiary backbone carbons, respectively, and C_i corresponds to the *i*th carbon from the branch chain end.

The assignment of spectral lines of S-34 copolymer is collected in Table 1.

Table 1. Assignment of spectral lines of S-34 copolymer

Line	Type	Sequence	Chemical Shift	Line	Type	Sequence	Chemical Shift
1	S _{αα}	BBBB		13	S _{δδ}	BEEE(B ⁰ γE)	29.937
2	S _{αα}	BBBE		14	CH ₂	BBB	
3	T _{δδ}	EBE	39.601	15	CH ₂	BBB	
4	S _{αα}	EBBE		16	S _{βγ}	BEE(B ⁰ γE)	27.248
5	T _{βδ}	BBE		17	CH ₂	EBB+S _{βδ} (BBEE)	
6	T _{ββ}	BBB		18	CH ₂	EBE	26.640
7	S _{αγ}	BBEB		19	S _{ββ}	EBEBE	
8	S _{αγ}	EBEB		20	S _{ββ}	BBEBE	
9	S _{αδ}	BBEE		21	S _{ββ}	BBEBB	
10	S _{αδ}	EBEE	33.984	22	CH ₃	EBE	11.116
11	S _{γγ}	BEEB		23	CH ₃	BBE	
12	S _{γδ}	BEEE(B ⁰ γE)	30.421	24	CH ₃	BBB	

Ethylene/1-Hexene Copolymer (S-43)

The ¹³C-NMR spectrum of S-43 is shown in Fig. 2. The numbering scheme and the nomenclature used are the same as that used in Ethylene /1-butene. The assignment of spectral lines is collected in Table 2.

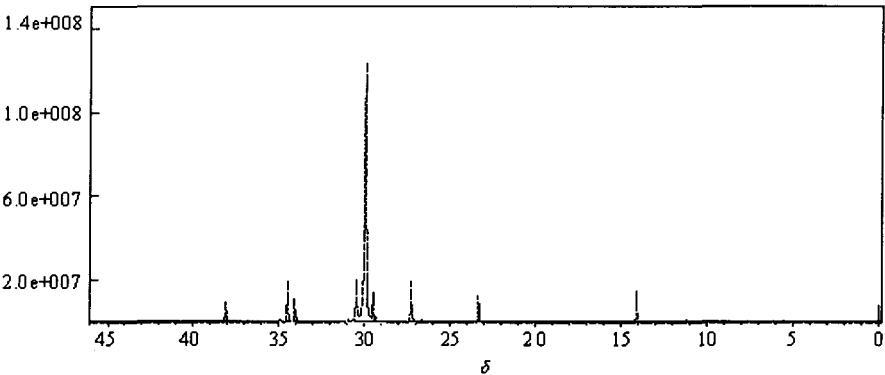


Fig. 2 ¹³C-NMR of S-43 (T=383K)

Calculation of Comonomer Sequence Distribution

The computational scheme for the comonomer sequence distribution obtained by Cheng^[4] was used to calculate the comonomer sequence distribution (mol%) of S-34 and S-43 copolymers. The

results are tabulated in Table 3.

Table 2. Assignment of spectral lines of S-43 copolymers

Line	Type	Sequence	Chemical shifts S-43	Line	Type	Sequence	Chemical shifts S-43
1	$S_{\alpha\alpha}$	HHHH	38.0843	9	$S_{\alpha\delta}$	EHEE	34.486
2	$S_{\alpha\alpha}$	HHHE			B_4	HHHEX	
3	$S_{\alpha\alpha}$	EHHE			B_4	EHHEX	
4	$T_{\delta\delta}$	EHE		12	$S_{\gamma\gamma}$	HEEH	
5	$T_{\beta\delta}$	HHE		13	$S_{\gamma\beta}$	HEEEH	30.446
6	$S_{\alpha\gamma}$	HHEH		14	$S_{\delta\delta}$	$HE_{n>3}H$	29.954
7+8+8a	B_4	HHHHH	34.945	15, 16, 17	B_3	H	29.475
	$S_{\alpha\gamma}$	EHEH		18, 19	$S_{\beta\delta}$	XHEE	27.053
	B_4	HHHHE		20, 21, 22	$S_{\beta\beta}$	HEH	
	$S_{\alpha\delta}$	HHEE		23	B_2	H	23.332
	B_4	EHHHE		24	B_1	H	14.070

The total number of 1-butene runs per average molecule, N is given by:

$$[N] = [BEB] + 1/2 [BEE]$$

The run number per 100 structural units, $\bar{N}$ as defined by Harwood is:

$$\bar{N} = [(BEB) + 1/2(BEE)] \times 100$$

The average comonomer sequence lengths of ethylene and butene units, $\bar{n}$ and $\bar{n}_B$ are given by:

$$\bar{n}_B = [B] / N \qquad \bar{n} = [E] / N$$

The run number and average comonomer sequence lengths of each type of unit for S-34 and S-43 are calculated and tabulated in Table 3.

Table 3. Comonomer sequence distribution (mol%)

Sequence	S-34 (%)	Sequence	S-43 (%)	Sequence	S-34 (%)	Sequence	S-43 (%)
[B]	3.9	[H]	4.0	[BEB]	0.0	[HEH]	0.0
[E]	96.1	[E]	96.0	[BEE]	7.8	[HEE]	8.1
[BB]	0.0	[HH]	0.0	[EEE]	88.3	[EEE]	87.8
[BE]	7.8	[HE]	8.1	Run No.	3.9		4.1
[EE]	92.2	[EE]	91.9	100[B]	3.9		4.0
[BBB]	0.0	[HHH]	0.0	100[E]	96.1		96.0
[BBE]	0.0	[HHE]	0.0	η_B	1.0	η_H	0.97
[EBE]	3.9	[EHE]	4.1	η_E	24.6	η_E	24.0

The results indicated that these copolymers synthesized by SINOPEC’s “metallocene adduct” technology contain small amounts of butene and hexene, and the EE and EEE sequences are dominant. The average comonomer sequence lengths of ethylene units for metallocene-based S-34 and S-43 are much longer than that of the butylene and hexene units. The comonomer sequence distributions of S-34 and S-43 are quite different from that of typical ethylene/1-butene and ethylene/1-hexene copolymers. The ethyl branches in ethyl /1-butene and butyl branches in ethyl/ 1-hexene low density polyethylene are all isolated branches.

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