

^{13}C -NMR STUDY OF ETHYLENE-1-OCTENE COPOLYMERS*

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ABSTRACT

A ^{13}C -NMR method is presented for a quantitative determination of the respective monomer composition and sequence distributions in ethylene-1-octene copolymers prepared with supported titanium/magnesium catalyst. On the basis of the sequence distributions, the ethylene-1-octene copolymerization mechanism was studied. It was found that the observed sequence distributions in ethylene-1-octene copolymers are satisfactorily predicted by the two-site model M/M, in which the copolymerization proceeds according to first-order Markovian statistics at the two different sites.

INTRODUCTION

It is well known that the density of polyethylene can be controlled through incorporation of a low amount of 1-olefin, which maintains polymer chain linearity in an overall configurational sense but leads to short chain branches. The linear 1-olefins 1-butene^[1-2], 1-hexene^[3-4] and 1-octene^[5] are commercially important for this purpose and result in ethyl, butyl, and hexyl branches in the respective copolymers. These chain branches randomly spaced along the polymer backbone and may exist as isolated branches or as "cluster" such as 1,3-dialkyl branches, 1,3,5-trialkyl branches, and so on. In industry, it is very important to control the monomer sequence distributions which have a close relation with the properties of such copolymers. To reach the point of control, first of all, a method should be established to determine the monomer sequence distributions in the copolymers, secondly, detailed investigation on the ethylene-1-olefin copolymerization mechanism has to be performed.

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^{13}C -NMR is the most powerful analytical method to evaluate the monomer sequence distributions in such copolymers. So far, many studies have been performed to deal with ethylene-propylene^[6-8], ethylene-1-butene,^[9-10] and ethylene-1-hexene^[11] copolymers. A number of authors^[6-8] have attempted to obtain information on the nature of ethylene-1-olefin copolymerization mechanism with heterogeneous Ziegler-Natta catalyst systems based on the sequence distributions.

In this work, the ^{13}C -NMR spectroscopy was applied to the determination of sequence distributions in ethylene-1-octene copolymers. On the basis of the monomer distributions, the peculiarity in copolymerization in the presence of $\text{TiCl}_4/\text{MgCl}_2\text{-AlR}_3$ was discussed.

EXPERIMENTAL

Materials

TiCl_4 , AlEt_3 and $\text{Al}(\text{i-Bu})_3$ were commercially obtained and used without further purification. Polymerization grade ethylene was purified by passing through a series of columns to remove residual traces of moisture and oxygen. MgCl_2 , a commercial anhydrous compound, was dried in an oven at 723K under HCl atmosphere for 6h to reduce the hydroxy content to almost zero. 1-Octene was refluxed over metallic sodium for 4h, distilled in vacuum and purged with dry nitrogen prior to use. $\text{TiCl}_4/\text{MgCl}_2$ catalyst was prepared as described in reference [5], by supporting TiCl_4 over highly dispersed MgCl_2 with a surface area of $85\text{m}^2/\text{g}$.

Polymerization

Copolymerization of ethylene with 1-octene was performed in a 0.5L autoclave in n-heptane medium with intensive mixing at 30°C . The constancy of the monomer concentrations during the copolymerization was controlled by chromatographically measurements. The reaction was stopped by the addition of ethanol.

^{13}C -NMR measurement: ^{13}C -NMR spectra were obtained at 125°C with a 75.5 MHz Bruker MSL-300 Fourier transform spectrometer. The ethylene-1-octene copolymers (EOC) samples were prepared as 0.05–0.15 g/ml solutions in o-dichlorobenzene with deuterodichlorobenzene- d_4 to main an internal lock signal.

RESULTS AND DISCUSSION

1. Determination of sequence distributions

One typical ^{13}C -NMR spectrum of ethylene-1-octene copolymer (EOC) is given in Fig. 1. It is found that the spectrum is complex, containing overlapping peaks. The complete assignments are shown in Table 1. The nomenclature system are the same as those reported by Carman et al. [12], where S and T refer respectively to the methylene and the methine carbons, and the Greek subscripts refer to the next nearest tertiary carbon. The hexyl branch carbon are numbered consecutively starting with the methyl as C_1 .

Table 1 Spectral assignments for ethylene-1-octene copolymer

Chemical shift	Backbone carbons		Branch carbons
	Methylene	Methine	
41.22	$\text{S}_{\alpha\alpha}(\text{OOOO})$	—	—
40.65	$\text{S}_{\alpha\alpha}(\text{OOOE})$	—	—
40.04	$\text{S}_{\alpha\alpha}(\text{EOOE})$	—	—
38.35	—	$\text{T}_{\beta\beta}(\text{EOE})$	—
36.11	—	$\text{T}_{\beta\beta}(\text{OOE})$	$\text{C}_6(\text{OOO})$
35.18	$\text{S}_{\alpha\gamma}(\text{OEO})$	—	$\text{C}_6(\text{OOE})$
34.70	$\text{S}_{\alpha\delta}(\text{OEE})$	—	$\text{C}_6(\text{EOE})$
33.63	—	$\text{T}_{\beta\beta}(\text{OOO})$	—
32.21	—	—	C_3
30.91	$\text{S}_{\gamma\gamma}(\text{OEEO})$	—	—
30.50	$\text{S}_{\gamma\delta}(\text{OEEE})$	—	—
30.02	$\text{S}_{\delta\delta}(\text{EEE})$	—	C_4
27.38	$\text{S}_{\beta\beta}(\text{OEE})$	—	C_5
24.75	$\text{S}_{\beta\beta}(\text{OEO})$	—	—
22.90	—	—	C_2
14.02	—	—	C_1

From Table 1, it is seen that comonomer dyad and triad sequence distributions are difficult to be obtained because of the spectral overlap. However, enough information is available from the spectrum by using a

quantitative procedure reported by Randall^[10] for ethylene-1-butene copolymer. As shown in Fig. 1, the spectrum of the EOC are divided into ten regions, defined as A-I. Utilizing regions A, B, D, F, G, H, and some necessary relationships, one can readily derive the following equations for the relative triad concentrations:

$$EEE = 1/4(2T_F + T_D - T_G - T_B)$$

$$EEO = (T_G + T_D - T_B - 2T_A)$$

$$OEO = T_H$$

$$EOE = T_B$$

$$OOE = 2(T_A - T_D)$$

$$OOO = T_D$$

where $T_A - T_H$ stand for the total area of regions A-H respectively.

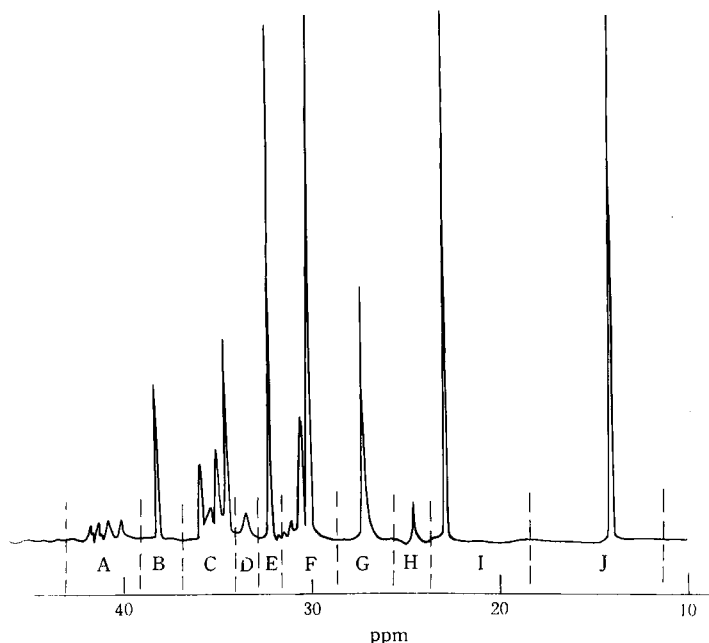


Fig. 1 Typical ^{13}C -NMR spectrum of ethylene-1-octene copolymer

Thus, the dyad distributions can be obtained by the Bovey's relationships^[13]:

$$EE = EEE + 1/2EEO$$

$$EO = 2EOE + OOE = 2OEO + EEO$$

$$OO = OOO + 1/2OOE$$

The monomer composition can be calculated from the triad distributions by

the equations:

$$\text{O} = \text{OOO} + \text{OOE} + \text{EOE}$$

$$\text{E} = \text{EEE} + \text{EEO} + \text{OEO}$$

From the dyad distributions, the monomer reactivity ratios can also be calculated by equations:

$$r_1 = 2 \text{ EE/EO } x$$

$$r_2 = 2 \text{ OO } x/\text{EO}$$

where $x = (\text{feed ethylene})/(\text{feed 1-octene})$

Observed copolymer composition, dyad distributions, triad distributions, and reactivity ratios for a series of three EOCs are given in Table 2. The monomer reactivity ratios determined by the Fineman-Ross method are as follows: for catalyst $\text{TiCl}_4/\text{MgCl}_2\text{-AlEt}_3$, $r_1 = 105$, $r_2 = 0.01$, and for catalyst $\text{TiCl}_4/\text{MgCl}_2\text{-Al(i-Bu)}_3$, $r_1 = 86.0$, $r_2 = 0.01$. Comparing the values of r_1 and r_2 found by these two methods, it can be seen that these data differ with each other quite appreciably. The authors believe that the copolymer inhomogeneity is responsible for the discrepancy.

Table 2 Monomer composition, sequence distributions, and monomer reactivity ratios of ethylene-1-octene copolymers

Sample	1	2	3
E	0.809	0.857	0.873
O	0.191	0.143	0.127
EE	0.713	0.772	0.782
EO	0.191	0.168	0.184
OO	0.096	0.060	0.034
EEE	0.645	0.701	0.713
EEO	0.136	0.142	0.138
OEO	0.028	0.013	0.023
EOE	0.049	0.050	0.070
OOE	0.093	0.068	0.044
OOO	0.049	0.025	0.013
r_1	87.0	89.1	65.8
r_2	0.086	0.074	0.048

Catalyst: samples 1 and 2— $\text{TiCl}_4/\text{MgCl}_2\text{-AlEt}_3$

sample 3— $\text{TiCl}_4/\text{MgCl}_2\text{-Al(i-Bu)}_3$

2. Copolymerization mechanism based on the sequence distributions

a. Single-site model

For copolymers produced by a single catalyst species, the triad distributions calculated for perfect Bernoullian and first-order Markovian distributions are compared in Table 3 with the observed one. It can be found that a Bernoullian statistical model is not applicable to predict the sequence distributions in EOCs. A first-order Markovian model provides good fits for O-centered triad sequence distributions, while this model provides larger values for OEE triad and smaller values for EEE triad in copolymers 1 and 2. These results indicate the existence of a second site which preferentially polymerizes ethylene, since the large values of the observed EEE triad correspond to the existence of the longer ethylene sequences than that predicted by a first-order Markovian model.

Table 3 Triad distributions predicted by Bernoullian(B) and/or first-order Markovian(M) statistical models

Samples		EEE	EEO	OEO	EOE	OOE	OOO
1	obsd.	0.645	0.136	0.028	0.049	0.093	0.048
	calcd. (B)	0.529	0.250	0.030	0.125	0.059	0.007
	calcd. (M)	0.629	0.167	0.011	0.048	0.096	0.048
2	obsd.	0.701	0.142	0.013	0.050	0.068	0.025
	calcd. (B)	0.629	0.021	0.018	0.105	0.035	0.003
	calcd. (M)	0.698	0.149	0.008	0.049	0.070	0.025
3	obsd.	0.713	0.138	0.023	0.070	0.044	0.013
	calcd. (B)	0.665	0.149	0.014	0.097	0.028	0.002
	calcd. (M)	0.699	0.166	0.010	0.050	0.066	0.009

b. Two-site model

Recently, Hayashi and coworker^[6] found that, the ¹³C-NMR data of ethylene-propylene copolymers have been shown to be consistent with two-site models. For ethylene-1-octene copolymers, the theoretical expression of two-site Bernoullian/Bernoullian (B/B), first-order Markovian/first order

Markovian (M/M), and first-order Markovian/Bernoullian (M/B) triad sequences are summarized in Table 4. The parameters of model M/M (or B/B) are the probabilities $P_{ee,i}$ and $P_{oo,i}$ (or P_{ei}) at two different sites and

Table 4 Theoretical expressions for comonomer sequence triads for B/B and M/M models

B/B model

$$\text{EEE} = W_1 P_{e1}^3 + W_2 P_{e2}^3$$

$$\text{EEO} = 2W_1 P_{e1}^2 P_{o1} + 2W_2 P_{e2}^2 P_{o2}$$

$$\text{OEO} = W_1 P_{e1} P_{o1}^2 + W_2 P_{e2} P_{o2}^2$$

$$\text{EOE} = W_1 P_{e1}^2 P_{o1} + W_2 P_{e2}^2 P_{o2}$$

$$\text{OOE} = 2W_1 P_{e1} P_{o1}^2 + 2W_2 P_{e2} P_{o2}^2$$

$$\text{OOO} = W_1 P_{o1}^3 + W_2 P_{o2}^3$$

M/M model

$$\text{EEE} = W_1 P_{ee,1}^2 P_{oe,1} + W_2 P_{ee,2}^2 P_{oe,2}$$

$$\text{EEO} = 2W_1 P_{ee,1} P_{oe,1} P_{oe,1} + 2W_2 P_{ee,2} P_{oe,2} P_{oe,2}$$

$$\text{OEO} = W_1 P_{eo,1}^2 P_{oe,1} + W_2 P_{eo,2}^2 P_{oe,2}$$

$$\text{EOE} = W_1 P_{eo,1} P_{oe,1}^2 + W_2 P_{eo,2} P_{oe,2}^2$$

$$\text{OOE} = 2W_1 P_{eo,1} P_{oe,1} P_{oo,1} + 2W_2 P_{eo,2} P_{oe,2} P_{oo,2}$$

$$\text{OOO} = W_1 P_{eo,1} P_{oo,1}^2 + W_2 P_{eo,2} P_{oo,2}^2$$

W_1, W_2 : mole fraction ($W_1 + W_2 = 1$)

P_{ei}, P_{oi} : Bernoullian probabilities of E and O respectively,

$P_{ee,i}/P_{oe,i}/P_{eo,i}/P_{oo,i}$ are the conventional 1st-order Markovian probabilities for E(e) and O(o)

the mole fraction W_i of the copolymer at one of the sites. The optimization of the parameters in these models was performed by the computerized simplex algorithm technique^[14-15]. By comparison between the observed and calculated sequence distributions (Table 5), it is found that only model M/M, in which the copolymerization mechanism obeys the respective first-order Markovian statistics at both sites, provides satisfactory fits. It is suggested that model M/M is an appropriate statistical model to describe the ethylene-1-octene copolymerization mechanism with the $\text{TiCl}_4/\text{MgCl}_2\text{-AlR}_3$ catalyst systems.

Table 5 Triad distributions in ethylene-1-octene copolymers predicted by two-site models

Samples		EEE	EEO	OEO	EOE	OOE	OOO
1	obsd.	0.645	0.136	0.028	0.049	0.093	0.049
	B/B	0.615	0.172	0.037	0.086	0.074	0.016
	B/M	0.645	0.136	0.027	0.052	0.089	0.050
	M/M	0.645	0.136	0.028	0.049	0.093	0.049
2	obsd.	0.702	0.142	0.013	0.050	0.068	0.025
	B/B	0.702	0.114	0.034	0.057	0.068	0.025
	B/M	0.701	0.142	0.009	0.052	0.057	0.039
	M/M	0.702	0.142	0.013	0.050	0.068	0.025
3	obsd.	0.713	0.137	0.024	0.070	0.044	0.013
	B/B	0.705	0.149	0.022	0.074	0.043	0.007
	B/M	0.711	0.155	0.018	0.077	0.035	0.004
	M/M	0.713	0.137	0.024	0.070	0.044	0.013

Keywords:

Ethylene-1-Octene copolymer; Sequence distribution; ^{13}C NMR

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