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Studies on the microstructure of ethylene/1-hexene copolymers prepared over heterogeneous Ziegler—Natta catalysts

Summary — Three $\text{MgCl}_2(\text{THF})_2$ -supported, AlEt_2Cl -activated VOCl_3 , VCl_4 and TiCl_4 Ziegler—Natta catalysts were used to copolymerize ethylene with 1-hexene in the presence of hydrogen to prepare low- M well-soluble copolymers that could be analyzed by ^{13}C -NMR. The spectra (Fig. 1) showed resonance signals due to ethylene and 1-hexene units in positions unaffected by catalyst type and with intensities related to the degree of comonomer incorporation into the copolymer. The triad sequence distribution and comonomer reactivity ratios (r) were calculated by the Randall method [11] and Bernoulli statistics based on the known copolymer composition. The latter appeared to be the more valid in predicting the comonomer triad distribution in the copolymer. All copolymers were found to be random ($r_E r_H \cong 1$) (Tables 4, 5). Compared with titanium, vanadium catalysts provided the higher monomer reactivity of ethylene toward α -olefin.

Key words: ethylene/1-hexene copolymers, $\text{MgCl}_2(\text{THF})_2$ -supported V and Ti catalysts, microstructure, reactivity coefficients.

The fraction of polyethylenes sold as a true homopolymer is relatively small, about 35% [1]. Copolymerization of ethylene with other co-monomers is of utmost importance for the total polyethylene business. Decreased regularity of the polyethylene chain results in lower crystallinity, lower melting points and, what is especially important, in lower density. The mechanical properties such as stiffness and impact strength are also affected. It should be stressed, however, that the literature data concerning the copolymers of ethylene with longer α -olefins are limited in spite of the commercial importance of the copolymers.

Copolymerization of ethylene with longer-chain olefins is the most important process used mainly to decrease the density and to change other properties of polyethylene. The properties of copolymerization products are determined by their microstructure. The microstructure greatly depends on the type of α -olefin co-monomer as well as on the type of the catalytic system applied and polymerization conditions. Most reports describe the copolymerization of ethylene with long-chained α -olefins over titanium catalysts and metallocene systems; only few are concerned with vanadium catalysts [2—4].

We have found that the vanadium-based catalysts supported on $\text{MgCl}_2(\text{THF})_2$ offer high activity in ethylene polymerization [5, 6] and copolymerization with α -olefins and produce copolymers with higher co-

monomer contents than do titanium catalysts supported on the same MgCl_2 -THF complex [7, 8]. Unfortunately, the microstructure of the resulting copolymers could not be determined because of the ultra high molecular weight and very low solubility of the copolymerization products which made ^{13}C -NMR spectra impossible to record. Therefore, the composition of the copolymers was measured only by the modified IR method [9]. Then, the copolymerization was studied in the presence of hydrogen as a chain transfer agent which reduced the molecular weight of the resulting copolymers and thus enabled ^{13}C -NMR to be used to analyze them [10]. This paper presents results of a detailed analysis of the microstructure of ethylene/1-hexene copolymers obtained in the presence of hydrogen over vanadium as well as titanium catalysts supported on $\text{MgCl}_2(\text{THF})_2$.

EXPERIMENTAL

Catalyst preparation and copolymerization procedures were described elsewhere [10].

The structure of the copolymers was analyzed by ^{13}C -NMR spectroscopy. Spectra were recorded at 95°C by using a Varian, Unity Inova 300 spectrometer operated at 75 MHz. Samples were dissolved in 1,2,4-trichlorobenzene/benzene- d_6 .

$$k[\text{HHH}] = 2 T_A + T_B - T_C \quad (3)$$

$$k[\text{HEH}] = T_F \quad (4)$$

$$k[\text{HEE}] = 2 (T_G - T_A - T_F) \quad (5)$$

$$k[\text{EEE}] = 0.5 (T_A + T_D + T_F - 2 T_G) \quad (6)$$

where: k is the NMR constant.

Since signals corresponding to regions A and F did not appear in the NMR spectra of the ethylene/1-hexene copolymers, the triad concentrations were calculated both from the spectra and equations 1–6 (Table 3).

The triad distributions calculated as described above were compared with the distributions predicted by assuming the Bernoullian statistics to hold true and based on the copolymer compositions obtained from the relative areas of different carbon resonances (Table 3). The results for all the copolymers showed the observed fraction of isolated co-monomer units in triads (EHE) to be lower than that predicted by the Bernoullian statistics. The concentration of the triads containing pairs of the co-monomer units (EHH) is higher than predicted, i.e., the copolymers appear to be blocky. These observations are similar to those of Randall [11] for ethylene/1-hexene copolymerization synthesized over an undefined catalyst.

The differences between the observed triad distributions and those calculated by the first-order Markovian scheme have also been confirmed by Ko [14] for ethylene/1-hexene copolymers prepared over a thermally pretreated $\text{MgCl}_2/\text{THF}/\text{TiCl}_4$ bimetallic catalyst. In contrast to the results mentioned above, the triad distribution showed the observed fraction of triads containing

isolated hexane units to be similar or higher than that calculated by the first-order Markovian statistics. Similar differences between the experimental concentration of these triads and that predicted by the Bernoullian statistics have also been obtained by Kimura [15] for ethylene/1-octene and ethylene/4-methyl-1-pentene copolymers prepared over a supported titanium catalyst. The latter observations are rather surprising in view of the fact that Ko's [14] experimental concentration of triads with pairs of the co-monomer units was also higher than predicted.

A triad distribution is sufficient to characterize co-monomer mole fractions, run numbers, average sequence lengths and their inverse defined as the "monomer dispersity" [11].

$$[E] = [\text{EEE}] + [\text{HEE}] + [\text{HEH}] \quad (7)$$

$$[H] = [\text{HHH}] + [\text{EHH}] + [\text{EHE}] \quad (8)$$

$$[N] = 0.5 [HE] = [\text{EHE}] + 0.5 [\text{EHH}] = [\text{HEH}] + 0.5 [\text{HEE}] \quad (9)$$

$$[\text{RN}] = 100 [N] \quad (10)$$

$$L_E = [E]/[N] \quad (11)$$

$$L_H = [H]/[N] \quad (12)$$

$$MD = 100 [N]/[H] = [\text{RN}]/[H] \quad (13)$$

where: $[E]$ and $[H]$ — mole fractions of ethylene and hexene, respectively, $[N]$ — total number of 1-hexene runs per average molecule, $[\text{RN}]$ — run number, L_E and L_H — average sequence lengths for each type of unit, respectively, MD — "monomer dispersity".

Table 3. Triad fraction (mole fraction) and structural parameters characterizing the ethylene/1-hexene copolymers obtained over $\text{MgCl}_2(\text{THF})_2/\text{precursor}/\text{Et}_2\text{AlCl}$ catalyst

| Precursor | $[\text{C}_6]$ ¹⁾ mol/dm ³ | model ²⁾ | [EHE] | [EHH] | [HHH] | [HEH] | [HEE] | [EEE] | [H] | [E] | [N] | L_H | L_E | MD |
|-----------------|---|---------------------|--------|--------|--------|--------|--------|--------|-------|-------|--------|-------|-------|------|
| VOCl_3 | 0.432 | exp | 0.0105 | 0.0222 | 0.0000 | 0.0000 | 0.0432 | 0.9241 | 0.033 | 0.967 | 0.0215 | 1.52 | 45.1 | 65.6 |
| | | B | 0.0136 | 0.0004 | 0.0000 | 0.0002 | 0.0272 | 0.9586 | 0.014 | 0.986 | 0.0138 | 1.01 | 71.4 | 98.6 |
| | 0.820 | exp | 0.0140 | 0.0290 | 0.0000 | 0.0000 | 0.0570 | 0.9000 | 0.043 | 0.957 | 0.0285 | 1.51 | 33.6 | 66.3 |
| | | B | 0.0192 | 0.0008 | 0.0000 | 0.0004 | 0.0384 | 0.9412 | 0.020 | 0.980 | 0.0196 | 1.02 | 50.0 | 98.0 |
| VCl_4 | 0.432 | exp | 0.0146 | 0.0236 | 0.0000 | 0.0000 | 0.0528 | 0.9089 | 0.038 | 0.962 | 0.0264 | 1.45 | 36.4 | 69.1 |
| | | B | 0.0256 | 0.0014 | 0.0000 | 0.0007 | 0.0512 | 0.9212 | 0.027 | 0.973 | 0.0263 | 1.03 | 37.0 | 97.4 |
| | 0.820 | exp | 0.0277 | 0.0111 | 0.0000 | 0.0000 | 0.0665 | 0.8946 | 0.039 | 0.961 | 0.0333 | 1.17 | 28.9 | 85.7 |
| | | B | 0.0299 | 0.0020 | 0.0000 | 0.0010 | 0.0598 | 0.9070 | 0.032 | 0.968 | 0.0309 | 1.04 | 31.3 | 96.6 |
| TiCl_4 | 0.432 | exp | 0.0109 | 0.0040 | 0.0000 | 0.0000 | 0.0258 | 0.9593 | 0.015 | 0.985 | 0.0129 | 1.16 | 76.3 | 86.5 |
| | | B | 0.0136 | 0.0004 | 0.0000 | 0.0002 | 0.0272 | 0.9586 | 0.014 | 0.986 | 0.038 | 1.01 | 71.4 | 98.6 |
| | 0.820 | exp | 0.0117 | 0.0040 | 0.0000 | 0.0000 | 0.0274 | 0.9569 | 0.016 | 0.984 | 0.0137 | 1.15 | 71.8 | 87.2 |
| | | B | 0.0127 | 0.0003 | 0.0000 | 0.0001 | 0.0254 | 0.9615 | 0.013 | 0.987 | 0.0128 | 1.02 | 77.1 | 98.5 |

¹⁾ $[\text{C}_6]$ — 1-hexene concentration in the feed, ²⁾ exp — triad distribution measured according to Randall model, B — triad distribution predicted via Bernoullian statistics.

Table 4. Diad distribution (mole fraction) and copolymerization parameters calculated from the triad distribution by using eqs. 14–20

| Precursor | [C ₆] ^{*)} mol/dm ³ | model ^{**)} | [EE] | [EH] | [HH] | [H] | [E] | P _{EE} | P _{EH} | P _{HE} | P _{HH} | r _E | r _H | r _E r _H |
|-------------------|--|----------------------|--------|--------|---------|-------|-------|-----------------|-----------------|-----------------|-----------------|----------------|----------------|-------------------------------|
| VOCl ₃ | 0.432 | exp | 0.9457 | 0.0432 | 0.0111 | 0.033 | 0.967 | 0.9780 | 0.0220 | 0.6636 | 0.3364 | 44.4545 | 0.5069 | 22.53 |
| | | B | 0.9722 | 0.0276 | 0.0002 | 0.014 | 0.986 | 0.9860 | 0.0140 | 0.9857 | 0.0143 | 70.4286 | 0.0145 | 1.02 |
| | 0.820 | exp | 0.9286 | 0.0570 | 0.0145 | 0.043 | 0.957 | 0.9703 | 0.0297 | 0.6628 | 0.3372 | 32.6700 | 0.5088 | 16.62 |
| | | B | 0.9604 | 0.0392 | 0.0004 | 0.020 | 0.980 | 0.9800 | 0.0200 | 0.9800 | 0.0200 | 49.0000 | 0.0204 | 1.00 |
| VCl ₄ | 0.432 | exp | 0.9353 | 0.0528 | 0.0118 | 0.038 | 0.962 | 0.9722 | 0.0278 | 0.6895 | 0.3105 | 34.9712 | 0.4503 | 15.75 |
| | | B | 0.9468 | 0.0526 | 0.0007 | 0.027 | 0.973 | 0.9731 | 0.0269 | 0.9741 | 0.0259 | 36.1384 | 0.0266 | 0.96 |
| | 0.820 | exp | 0.9279 | 0.0665 | 0.0056 | 0.039 | 0.961 | 0.9656 | 0.0344 | 0.8564 | 0.1436 | 28.0345 | 0.1677 | 4.70 |
| | | B | 0.9369 | 0.0618 | 0.0010 | 0.032 | 0.968 | 0.9679 | 0.0321 | 0.9688 | 0.0313 | 30.1263 | 0.0323 | 0.97 |
| TiCl ₄ | 0.432 | exp | 0.9722 | 0.0258 | 0.0020 | 0.015 | 0.985 | 0.9870 | 0.0130 | 0.8667 | 0.1333 | 75.9235 | 0.1538 | 11.68 |
| | | B | 0.9722 | 0.0276 | 0.0002 | 0.014 | 0.986 | 0.9860 | 0.0140 | 0.9857 | 0.0143 | 70.4490 | 0.0145 | 1.02 |
| | 0.820 | exp | 0.9706 | 0.0274 | 0.0020 | 0.016 | 0.984 | 0.9864 | 0.0136 | 0.8750 | 0.1250 | 72.4341 | 0.1429 | 10.35 |
| | | B | 0.9742 | 0.0257 | 0.00015 | 0.013 | 0.987 | 0.9870 | 0.0130 | 0.9885 | 0.0115 | 76.1070 | 0.0115 | 0.89 |

*) **) see Footnotes to Table 1

All the values calculated for the observed triad distributions and the corresponding parameters calculated for perfect Bernoullian distributions are given in Table 3.

According to Randall [11], the MD value of 100 would indicate that the 1-hexene units are all isolated in the copolymer chain as EHE sequences, but any value below 100 shows the tendency of co-monomer to form a continuous series or "clusters". This parameter appears to be a more sensitive indicator of deviation from the perfectly random distribution than either the run number or an examination of observed and calculated triad distributions. The present results indicate that each copolymer, regardless of the catalytic system used, is the least random copolymer (MD < 99). It should be stressed, however, that monomer dispersity values calculated from the observed triad distribution are clearly lower than those predicted by the Bernoullian distribution. Especially large differences are noticed for the copolymer obtained in the presence of vanadium catalysts. These results lead to the conclusion that, in these systems, 1-hexene exhibits the tendency of forming more "clusters" of the co-monomer units.

To verify these results, copolymerization parameters were calculated on the basis of the resulting triad concentrations and by using the following equations [14, 16, 17]:

$$[EE] = [EEE] + 0.5 [HEE] \quad (14)$$

$$[HH] = [HHH] + 0.5 [HHE] \quad (15)$$

$$[EH] = (2[EHE] + [HHE] + [HEE] + 2[HEH])/2 = 2[EHE] + [EHH] \quad (16)$$

$$P_{EE} = [EE]/[E] = 1 - P_{EH} \quad (17)$$

$$P_{HH} = [HH]/[H] = 1 - P_{HE} \quad (18)$$

$$r_E = P_{EE}/P_{EH} \quad (19)$$

$$r_H = P_{HH}/P_{HE} \quad (20)$$

where: P_{ij} is the probability of addition of monomer i to chain end j , and subscripts E and H refer to ethylene and 1-hexene, respectively, r_E and r_H are copolymerization reactivity ratios of ethylene and 1-hexene, respectively.

The necessary diad distribution and the reactivity ratios of comonomers are summarized in Table 4. The results show large differences between the reactivity ratios obtained over experimental and predicted sequence concentrations. Especially large divergences between the products of the reactivity ratios were confirmed. All these values obtained on the basis of the experimental triad concentrations — independently of the catalytic system used — are clearly higher than the predicted values. The sequence distribution of synthesized copolymers is thus inferred to be blocky. These observations are rather surprising if the low effective co-monomer incorporation (< 5 mol%) is taken into consideration. On the other hand, the values of the same products calculated for the perfect Bernoullian distributions are close to those indicating that each copolymer is random.

To verify the conformity of the results obtained by the two methods compared above, the co-monomer reactivity ratio products were calculated from eqs. 14–20 for the observed triad distributions and for the corresponding Bernoullian distributions obtained by Randall [11]. The results presented in Table 5 show the data calculated on the basis of these two methods to diverge,

Table 5. Diad distribution (mole fraction) and copolymerization parameters calculated from the triad distribution obtained by Randall for ethylene/1-hexene copolymers [11]

| [H], mol % | model ^{*)} | [EE] | [EH] | [HH] | [H] | [E] | P_{EE} | P_{EH} | P_{HE} | P_{HH} | r_E | r_H | $r_E r_H$ |
|------------|---------------------|--------|--------|---------|--------|--------|----------|----------|----------|----------|--------|--------|-----------|
| 1.9 | exp | 0.9623 | 0.0359 | 0.00095 | 0.0189 | 0.9807 | 0.9812 | 0.0188 | 0.9497 | 0.0503 | 52.30 | 0.053 | 2.77 |
| | B | 0.9623 | 0.0373 | 0.00035 | 0.0190 | 0.9810 | 0.9809 | 0.0191 | 0.9816 | 0.0184 | 51.457 | 0.0187 | 0.96 |
| 17.3 | exp | 0.7012 | 0.2502 | 0.0483 | 0.1734 | 0.8262 | 0.8487 | 0.1513 | 0.7215 | 0.2785 | 5.6096 | 0.3860 | 2.165 |
| | B | 0.6839 | 0.2861 | 0.02995 | 0.1730 | 0.8270 | 0.8270 | 0.1730 | 0.8269 | 0.1731 | 4.7791 | 0.2093 | 1.00 |

*) see Footnote to Table 1.

too. The ethylene/1-hexene copolymers seem to be blocky on the basis of Randall sequence distributions or random on the basis of the Bernoullian distribution. It is known from the literature [18, 19] that the intramolecular distribution of co-monomer (along the single molecular chain) in LLDPE is essentially Bernoullian. Therefore, a possible reason for the divergences observed can be the heterogeneity of the intermolecular distribution of copolymers, i.e. different compositions of each macromolecular chain independently from the random co-monomer distribution of each polyethylene chain. This is caused by the heterogeneity of active sites on the supported catalysts, as additionally confirmed by the high values of the molecular weight distributions of the copolymer obtained [10]. In order to investigate this problem, an intermolecular chemical co-monomer distribution of the ethylene/ α -olefin copolymers obtained over different catalytic systems will be studied by fractionation, and the microstructure of whole polymers as well as their fractions will be compared.

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