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A pre-metallocene single-site catalyst for olefin polymerization: the $V(acac)_3$ - Al*i*-Bu_2Cl system

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Summary

A combination of GPC, DSC, and ^{13}C NMR data for an ethylene/1-hexene copolymer prepared with the $V(acac)_3$ - Al*i*-Bu_2Cl system at 5°C shows that this catalyst system was one of the earliest pre-metallocene catalysts for olefin polymerization.

Introduction

The term "single-site catalysts" was coined soon after Kaminsky and Sinn discovered the first highly active metallocene catalysts, combinations of zirconocene complexes and methylalumoxane (MAO) [1,2]. These catalysts, when used at high [MAO]:[zirconocene] ratios, have only one type of active centers. As a result, they produce polymers with a narrow molecular weight distribution (M_w/M_n ~2.0), which can be described by a single Flory molecular weight distribution function [3-5]. When α-olefin copolymers are prepared with the metallocene catalysts, they have very narrow compositional distributions, as indicated by their narrow temperature-rising elution fractionation (TREF) and crystallization fractionation (Crystaf) curves, narrow melting peaks, and depressed melting points [5-a,6].

However, single-site polymerization catalysis is not the exclusive domain of Kaminsky-Sinn systems. Several earlier polymerization catalysts also have features which could justify their definition as single-site catalysts. The best known of them is the early metallocene catalyst Cp_2TiCl_2 - AlR_2Cl developed by Natta and Breslow [7]. Judging by the molecular weight distribution analysis of ethylene/propylene copolymers prepared with this catalyst, it also qualifies as a single-site system [8]. Another well-known group of single-site catalyst systems is based on VCl_4. When catalysts such as VCl_4 - AlR_2Cl or VCl_4 - $Al_2R_3Cl_3$ are used for copolymerization of ethylene and propylene at ambient temperatures, they also produce polymer materials with narrow molecular weight distributions [9,10], which can be described by a single Flory molecular weight distribution function [4].

Another potential single-site system is one of the earliest catalysts used for ethylene polymerization, the hydrocarbon-soluble $V(acac)_3$ - Al*i*-Bu_2Cl system. This catalyst system was often employed during the early days of the Ziegler-Natta epoch as an alternative to other vanadium-based systems for the synthesis of ethylene/propylene elastomers [11-13], ethylene/1-hexene elastomers [14], and amorphous polypropylene [15]. Ethylene/propylene copolymers prepared with this catalyst have a very narrow compositional distribution [13,16]. We decided to investigate the structure of an ethylene/1-hexene copolymer produced at low temperature with the V(acac)$_3$ - Al*i*-Bu$_2$Cl system and determine whether this catalyst qualifies as a single-site catalyst.

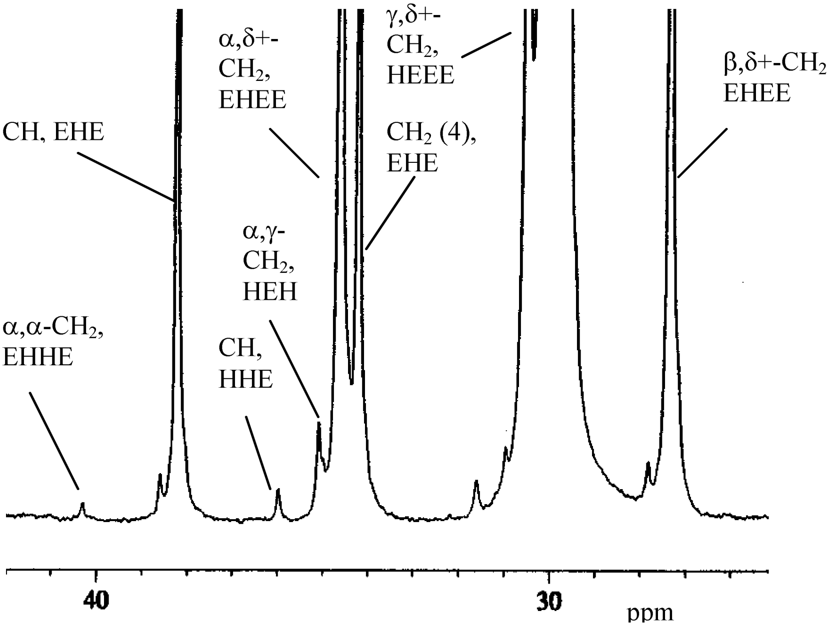

Figure 1. ^{13}C NMR spectrum of ethylene/1-hexene copolymer prepared with V(acac)$_3$ - Al*i*-Bu$_2$Cl system at 5°C

Experimental

Copolymerization reactions Copolymerization of ethylene and 1-hexene was carried out in a 500-mL stainless steel reactor equipped with a high-speed magnet-driven stirrer [14]. The reaction was performed at 5°C in a medium of pure 1-hexene without any inert diluents. The following amounts of the reactants were used: 1-hexene 200 mL, Al*i*-Bu$_2$Cl = 1.03 mmol, V(acac)$_3$ = 0.0157 mmol (as a 0.031 M solution in toluene). The polymerization reaction was initiated by adding the V(acac)$_3$ solution to the reactor and it continued for 20 min under an ethylene partial pressure of 8 MPa. The productivity of the catalyst system was 415 g/mmol V. The copolymer contained ~7.0 mol.% of 1-hexene and had density of 0.891 g/cc. Even at this low temperature, the V(acac)$_3$ - Al*i*-Bu$_2$Cl system exhibits unstable kinetic behavior: the ethylene consumption rate reaches a maximum at ~3 min after the V(acac)$_3$ introduction, it then rapidly decreases, and the catalyst system becomes completely inactive after 18-20 minutes, the behavior typical for most V-based polymerization catalysts [11,12,17]. For comparison purposes, several ethylene/1-hexene copolymers were prepared with the (*n*-Bu-Cp)$_2$ZrCl$_2$ - MAO system at 60°C using the same equipment.

Copolymer analysis GPC analysis of the copolymers was carried out in 1,2,4-trichlorobenzene at 145°C using a Waters 150C Liquid Chromatograph equipped with 4 columns of cross-linked styrene/divinylbenzene copolymer (2 columns 10^6, 10^4, and 10^3 A). The copolymer prepared with the $V(acac)_3$ - Al*i*-Bu_2Cl system has a high molecular weight, M_w = 695,000, and a narrow molecular weight distribution, $M_w/M_n = 1.8$. The Flory component analysis of the GPC curve was carried out with the Scientist program (MicroMath Scientific Software), as described earlier [3,4]. DSC melting curves of the copolymer were recorded using a TA Instruments 9900 Thermal Analyzer at a heating rate of 2°C/min. The ^{13}C NMR spectrum of the copolymer was recorded at 100.4 MHz on a JEOL GX400 NMR spectrometer at 130°C using appropriate experimental parameters for quantitative spectra of polyolefins. The sample was prepared as solution in a 3:1 mixture of 1,3,5-trichlorobenzene and 1,2-dichlorobenzene-d_4. The pulse angle was 90° and the pulse delay, 15 sec. Continuous ^1H decoupling was applied throughout the recording. The spectrum and the resonance assignments are shown in Fig. 1.

Results and discussion

Measurement of copolymer composition Earlier, Randall described a procedure for the composition evaluation of ethylene/1-hexene copolymers [18] by measuring relative contents of different triads, *EHE*, *HHE*, *HHH*, *HEH*, *EEH*, and *EEE* in ^{13}C NMR spectra. We developed a more straightforward approach to the composition measurement based on averaging of peak areas, thus minimizing the effect of peak overlap. The resonances from CH_3 groups (14-15 ppm) are always slightly attenuated due to their longer spin-lattice relaxation times; these peaks were not used. The total peak area in the range 22-43 ppm is proportional to the sum of the signals from the CH_2 groups in all ethylene units and from five out of six carbon atoms in the hexene units. For molar fractions of 1-hexene (C_H) and ethylene ($C_E = 1\text{-}C_H$), the total area in the 22-43 ppm range, A_{total}, is proportional to $5 \cdot C_H + 2 \cdot C_E = 2 + 3 \cdot C_H$. Only one resonance, at 22-24 ppm, is exclusively due to 1-hexene units; it arises from CH_2 groups next to methyl groups; whereas all other signals of 1-hexene units overlap with the resonances of ethylene units and/or with each other. The area of the resonance at 23.4 ppm is used as an unambiguous measure of the 1-hexene content: A(22-24 ppm) is proportional to C_H. Combining these two equations gives: $C_H = 2/[A_{total}/A(22\text{-}24\ \text{ppm}) - 3]$.

Estimation of r_1r_2 values Ethylene has a much higher reactivity in copolymerization reactions with transition metal catalysts compared to any α-olefin [5]. For example, the reactivity ratio r_1 for the ethylene/1-hexene pair ($V(acac)_3$ - Al*i*-Bu_2Cl catalyst) is higher than 40 [5-a,12]. Ethylene/α-olefin copolymers produced with homogeneous Ziegler-Natta catalysts belong to the group of random copolymers: monomer units of both types, ethylene (*E*) and an α-olefin (*Ol*), are statistically distributed in the copolymer chains. The degree of randomness in the distribution of monomer units is traditionally defined by the value of the product of reactivity ratios, r_1r_2 [5,16]. For example, if the r_1 value characterizing the reactivity of the α-olefin (and hence the r_1r_2 value) is equal to zero, the copolymer is alternating, with no *Ol* units attached to other *Ol* units (i.e., the copolymer chains contain no *Ol-Ol* diads, *Ol-Ol-Ol* triads, etc.). The case of $r_1r_2 = 1$ corresponds to a completely random copolymer governed by Bernoulli statistics, high r_1r_2 values indicate blocky copolymers and, if $r_1r_2 \rightarrow \infty$, every copolymer molecule would consist of only two homopolymer blocks, *~E-E-E-E~* and

~*Ol-Ol-Ol-Ol*~. The r_1r_2 values for ethylene/α-olefin copolymers usually vary from 0.1 to ~1 [5,16].

A reliable ^{13}C NMR-based estimation of r_1r_2 values for ethylene/1-hexene copolymers containing relatively low amounts of 1-hexene, from 5 to 20 mol.%, represents a challenge. Such estimations can be potentially based on the measurement of the relative contents of 1-hexene sequences of different lengths from their CH resonances or the relative content of *HH* diads from the CH_2 group between adjacent hexene units vs. the content of isolated 1-hexene units. However, as Fig. 1 shows, all the resonances attributed to 1-hexene blocks are quite small. The use of the signal areas of isolated 1-hexene units in copolymer chains as references, such as CH(*EHE*), CH_2(4)(*EHE*), or β,δ^+CH(*EHEE*), is also questionable due to large differences between the areas on any *HH* signal and any *EHE* signal.

These difficulties were avoided by using the following signal areas for the evaluation of the r_1r_2 value (see Fig. 1): the α,α-CH_2 resonance of the *EHHE* tetrad at 40.3 ppm, the CH resonance of the *EHH* triad at 35.9 ppm, and, as the reference, the β,β-CH_2 resonance of the *HEH* triad at 24.6 ppm. Statistically based equations for the relative populations of these sequences were presented earlier [5,16]: [*EHHE*]/[*HEH*] = $(r_1\mathrm{F})\cdot r_1r_2\cdot(1 + r_1\mathrm{F})/(r_1r_2 + r_1\mathrm{F})^2$ and [*HHE*]/[*HEH*] = $2\cdot(r_1\mathrm{F})\cdot r_1r_2/(r_1r_2 + r_1\mathrm{F})$, where the r_1F parameter is $0.5\cdot\{(C_E/C_H - 1) + [(C_E/C_H - 1)^2 + 4r_1r_2\cdot(C_E/C_H)]^{0.5}\}$. Both the [*EHHE*]/[*HEH*] and the [*HHE*]/[*HEH*] ratio are virtually independent of the copolymer composition ratio C_E/C_H but depend strongly on the r_1r_2 value.

Structure of ethylene/1-hexene copolymer produced with the V(acac)$_3$ - Ali-Bu$_2$Cl system In general, the fact that the M_w/M_n value for a given polymer is close to 2 cannot be regarded as a sufficient proof that the polymer is produced by a single type of active center. A comparison of the experimental molecular weight distribution curve in the GPC coordinates with the curve calculated for a single Flory function is a more reliable test [4,5a]. As Fig. 2 demonstrates, the molecular weight distribution of the copolymer produced with the V(acac)$_3$ - Ali-Bu$_2$Cl system can be indeed described by a single Flory distribution function with $M_w = 6.58\cdot10^5$. This fit is a distinct feature of polymers produced with single-site catalysts [3-5].

The copolymer contains 6.7 mol.% 1-hexene. The resonances from 1-hexene units linked together, such as the α,α-CH_2 resonance of the *EHHE* tetrad at ~40 ppm, the CH resonance of the *EHH* triad at 35.7 ppm, and the β,β-CH_2 resonance of the *HEH* triad in the 24.0-24.5 ppm range, are quite small (Fig. 1). This suggests that the monomer unit distribution has more alternating monomer sequences than predicted by random statistics. Estimation of the r_1r_2 value from the experimentally measured [*EHHE*]/[*HEH*] and [*HHE*]/[*HEH*] ratios gives r_1r_2 as ~0.30-0.35. (The only literature estimate of r_1r_2 for ethylene/1-hexene copolymerization with the V(acac)$_3$ - Al*i*-Bu$_2$Cl system at 0°C [12] reports an r_1r_2 value of ~0.57.) Our r_1r_2 evaluation indicates that the ethylene/1-hexene copolymer produced at 5ºC with the V(acac)$_3$ - Al*i*-Bu$_2$Cl system has a pronounced tendency to an alternating structure. This phenomenon is also found for ethylene/1-hexene copolymers prepared with single-site metallocene catalysts. A similar analysis of ethylene/1-hexene copolymers produced with the (*n*-Bu-Cp)$_2$ZrCl$_2$ - MAO system at 60°C gave r_1r_2 values in the range of 0.15-0.20.

The melting endotherm of the V(acac)$_3$ - Al*i*-Bu$_2$Cl copolymer is narrow, and the melting point is low, at 97.4°C for the nascent material and at 83.1°C for the pre-crystallized sample; this indicates that the copolymer has a narrow compositional distribution. Ethylene/1-hexene copolymers prepared with single-site metallocene

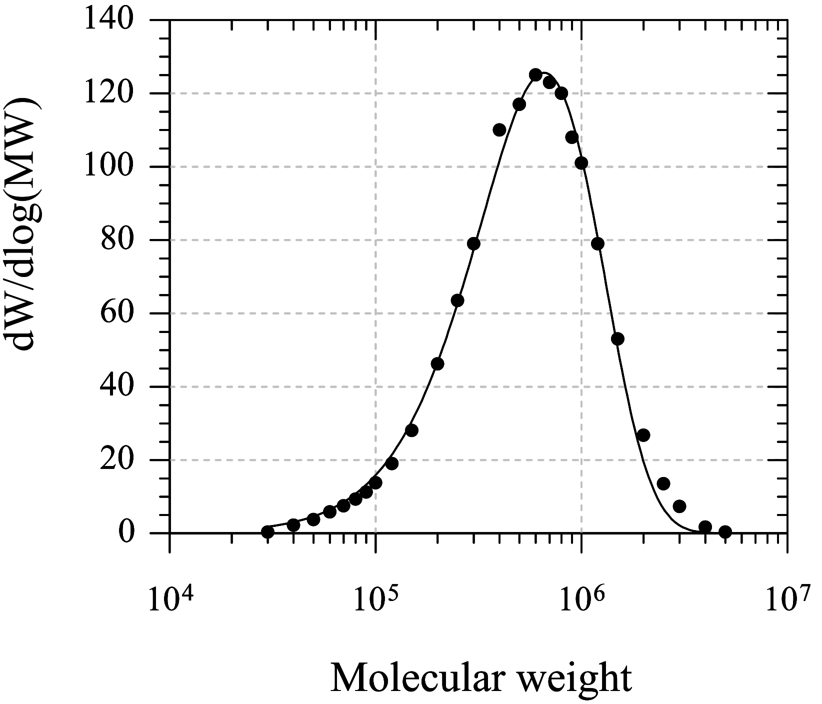

Figure 2. GPC curve of ethylene/1-hexene copolymer prepared with $V(acac)_3$ - Al*i*-Bu_2Cl system at 5°C. Solid line- GPC curve of a single Flory component with M_w=657,900

catalysts also have low melting points, from 106-110°C for copolymers containing 3.2 - 3.5 mol.% 1-hexene, to 91-94°C for copolymers containing 5.0 - 5.5 mol.% 1-hexene. In contrast, copolymers of the same composition produced with multi-center Ti-based catalysts have broad melting endotherms, and their effective melting points are much higher, from 127 to 123°C.

In conclusion, structural analysis of the ethylene/1-hexene copolymer prepared with the $V(acac)_3$ - Al*i*-Bu_2Cl catalyst showed that this system indeed exhibits all the attributes of a single-site catalyst: a narrow molecular weight distribution described by a single Flory function, a narrow compositional distribution, and a tendency to alternate monomer units in olefin copolymers. The only difference between the $V(acac)_3$-based catalyst and metallocene catalysts is in activity: under similar conditions, the activity of the metallocene catalysts is 100-200 times higher.

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