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Randomness in Ziegler–Natta olefin copolymerizations as determined by ^{13}C-NMR spectroscopy—the influence of chain heterogeneity

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Abstract

The chain heterogeneity of a polyethylene resin can be assessed by simple dissolution techniques followed by compositional analyses. This heterogeneity influences common measurements of the randomness of the polymerization process. Specifically, the values for the product of reactivity ratios and the relative monomer dispersities will suggest a less random polymerization process than is actually occurring on a molecular scale.

For the system studied, compositional analysis of the parent resins demonstrates the blockiness (non-random) character commonly reported for heterogeneous Ziegler–Natta polymerizations. Compositional analyses of the soluble and insoluble fractions show at least two chain populations with significantly different ethylene/1-hexene molar ratios, each showing a near random incorporation of comonomer. These data are consistent with at least two catalyst sites, each with different comonomer incorporation efficiency.

Keywords: Polyethylene; Fractionation; ^{13}C-NMR

1. Introduction

Polyethylene can be divided into three basic classes, low-density polyethylene (LDPE), high-density polyethylene (HDPE), and linear low-density polyethylene (LLDPE) [1]. LDPE is prepared at high pressure and contains a wide variety of branches. HDPE is prepared at lower temperatures using transition metal catalysts and has few branches. The final class, LLDPE, is prepared from ethylene and a comonomer, again generally using transition metal catalysts. They are characterized as having a relatively ‘high’ concentration of branches, e.g. 5–50 branches per 1000 carbons (or 1–10 mol% comonomer) [2].

It is a common practice to use carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectroscopy not only to differentiate between these polyethylene resin classes, but also to measure the comonomer content [2–4]. It is also quite common to use ^{13}C-NMR data to calculate parameters that provide information on the distribution (‘dispersity’) of the comonomers along the polymer backbone. Two of the more common parameters determined by NMR are the product of reactivity ratios and monomer dispersity (MD).

Reactivity ratios have a long history in polymerization chemistry [5]. Early experiments developed these ratios, and the product of these ratios, to monitor the chemistry of polymerizations. Simply put, a reactivity ratio is the rate of reaction of one monomer over the rate of reaction of a second monomer with the same polymerization site. In copolymerizations involving two monomers, there are two polymerization sites and four reaction rates.

Namely:

$$M_1^* + M_1 \underset{k_{11}}{\Rightarrow} M_1 - M_1^* \tag{1}$$

$$M_1^* + M_2 \underset{k_{12}}{\Rightarrow} M_1 - M_2^* \tag{2}$$

$$M_2^* + M_2 \underset{k_{22}}{\Rightarrow} M_2 - M_2^* \tag{3}$$

$$M_2^* + M_1 \underset{k_{21}}{\Rightarrow} M_2 - M_1^* \tag{4}$$

where M_1^* refers to an active polymerization site where monomer one was the last monomer to incorporate and M_2^*

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refers to an active polymerization site where monomer two was the last monomer to incorporate.

The reactivity ratios are:

$$r_1 = k_{11}/k_{12} \tag{5}$$

$$r_2 = k_{22}/k_{21} \tag{6}$$

The product of reactivity ratios (r_1r_2) can be used to access the 'character' of the copolymerization [6]. If $r_1r_2 > 1$ then the copolymer has a blocked character. If $r_1r_2 \approx 0$ then the copolymer has an alternating character. If $r_1r_2 = 1$ then the polymerization is random in character. Fundamentally, a polymer can either tend toward blockiness or tend toward alternating. The characterization of a polymer as being random is simply the absence of either blockiness or alternating character. Usami et al. have demonstrated how the product of reactivity ratios can be calculated from the results of ^{13}C-NMR compositional analyses [7].

A second parameter developed for the characterization of the distribution of comonomer is MD [8]. It has also been used as a measure of the randomness of copolymerizations. MD is nothing more than the ratio of the molar concentration of comonomer present as mixed dyads [EX] over the total molar concentration of comonomer.

$$\mathrm{MD} = 100 \times 0.5 \times [\mathrm{EX}]/[\mathrm{X}] \tag{7}$$

If all the comonomer was present as mixed dyads, then this value is equal to 100 and the comonomer is '100%' dispersed in the 'ethylene matrix'. To compare the MD between copolymers with different concentrations of comonomer, it is necessary to 'normalize' the MD. This is accomplished by dividing the MD by the molar concentration of ethylene, obtaining the relative monomer dispersity (RMD).

$$\mathrm{RMD} = \mathrm{MD}/[\mathrm{E}] \tag{8}$$

This simplifies to the ratio of observed concentration of mixed dyads over the concentration expected from Bernoulian (random distribution) statistics. A value of 100 is indicative of a random polymerization. A value less than 100 is indicative of a propensity toward blockiness and a value greater than 100 indicative of a propensity toward an alternating character.

In the last 10 years, it has become increasingly apparent that the distribution of the comonomer, e.g., short chain branches, contributes to the crystallization behavior and resulting properties [9–11] of polyethylene. Analytical efforts along these lines have included temperature rising elution fractionation (TREF), crystallization fractionation (Crystaf®), differential scanning calorimetry (DSC), and size exclusion chromatography coupled with Fourier transform infrared detection (SEC-FTIR) [12–15].

Each of these techniques provides information on the distribution of the branches within the polymer matrix, and more importantly demonstrates the presence of chain heterogeneity. For TREF, Crystaf®, and DSC, the separation is based on solubility or crystallinity. Polymer chains with higher comonomer content will dissolve first and crystallize last. As the name implies, SEC-FTIR performs a separation based on size. With appropriate cautions, the size is directly related to molecular weight and a comonomer distribution with molecular weight is obtained.

It will be the subject of this paper to examine the reactivity ratio products and relative monomer dispersities for a few Ziegler–Natta resins. The significance of these values for the parent resins, and for fractions obtained by simple solvent treatment of the resins will be discussed with respect to chain heterogeneity and the character of the Ziegler–Natta polymerization.

2. Experimental

Three ethylene/1-hexene copolymers were obtained from an ethylene polymerization pilot plant using a proprietary Ziegler–Natta based catalyst in a slurry loop process. The feed rates and activation parameters where varied to produce resins with 4–5 mol% 1-hexene. These resins were then subjected to simple solvent fractionation. This involved dissolution of each resin in 1,2,4-trichlorobenzene, containing 1% BHT, at 155 °C for 12 h in a convection oven. Each solution was gently rotated periodically to insure homogeneous dissolution and tightly capped (after 15 min at temperature) to minimize oxidation. After a uniform solution was achieved, the oven was turned off to allow the solution to cool to room temperature slowly, with a rate approximating 0.7 to 0.9 °C/min. The slurry was filtered using a filter with a pore diameter of 0.45 μm. The room temperature solubles were then obtained by evaporation of the filtrate in a vacuum oven. The residue left on the filter is defined as the room temperature insolubles.

Each parent resin and solvent fraction was analyzed by C-13 NMR spectroscopy following standard practices using a Varian Unity 300 spectrometer. This involved dissolution of the parent resin or fraction at 10 wt% in a 6:1 mixture of 1,2,4-trichlorobenzene and d$_4$-1,4-dichlorobenzene at 135 °C. The spectra were acquired at 125 °C using a 90° excitation pulse, a 10-s pulse delay, and full decoupling (for complete nOe) using a WALTZ-16 based decoupling pulse sequence. The sequence distribution analysis was performed following literature procedures [8].

3. Results and discussion

The results from the ^{13}C-NMR analyses of the three parents and their respective solvent fractions are shown in Table 1. Also included in the table are estimates for the properties of the parent resins based on the combined properties for the solvent fractions, weighted appropriately for the amount of each fraction obtained.

There are two striking features of these data, the

Table 1
^{13}C-NMR microstructural analysis of Ziegler–Natta resins

	Fractions		Parents	
	Solubles	Insolubles	Estimated	Exper.
Resin 250A				
wt% Resin	9.28%	90.06%		
mol%[H]	17.10%	2.59%	3.68%	3.65%
mol% [EHE]	12.51%	2.47%	3.22%	3.32%
mol% [HHE]	3.34%	0.13%	0.37%	0.27%
mol% [HHH]	1.25%	0.01%	0.10%	0.06%
r_1r_2	0.79	1.05	1.92	1.29
RMD	100%	100%	95.9%	98.3%
Resin 251				
wt% Resin	9.44%	89.29%		
mol%[H]	17.71%	2.30%	3.46%	3.55%
mol% [EHE]	12.68%	2.15%	2.95%	3.05%
mol% [HHE]	3.19%	0.15%	0.38%	0.36%
mol% [HHH]	1.13%	0.00%	0.09%	0.14%
r_1r_2	0.7	1.5	2.2	2.2
RMD	103%	99%	96%	95%
Resin 270B				
wt% Resin	11.19%	87.26%		
mol% [H]	19.31%	2.46%	3.95%	3.99%
mol% [EHE]	13.11%	2.25%	3.21%	3.20%
mol% [HHE]	4.50%	0.23%	0.61%	0.54%
mol% [HHH]	1.69%	0.00%	0.15%	0.25%
r_1r_2	0.9	2.0	2.9	3.0
RMD	99%	98%	92%	91%

'alternating' character and the high comonomer content (17–19 mol%) of the copolymer found in the solubles fraction. The r_1r_2 values for all the solubles fractions would classically be interpreted as indicating the copolymer in this fraction has an alternating character. The RMD values are less definitive with one resin having alternating character, one having blocked character, and one essentially random. However, in all cases, whether we look at r_1r_2 or RMD, the copolymer in the solubles fraction shows a greater alternating character than the parent resin. This alone would strongly suggest that the use of r_1r_2 and RMD (and any other like microstructural parameters) for characterization of a whole resin is inadvisable.

The composition of the insolubles fraction is nearly identical for all three resins, namely about 2.4 mol% 1-hexene (with the remainder being ethylene). For the insolubles fractions, the relative monomer dispersities ranged from 98 to 100, suggesting these polymer chains were formed via a nearly random polymerization process. This is contrasted by the product of reactivity ratios (r_1r_2), which varies from 1.05 to 2.0. Since any value over 1.0 indicates some blockiness to the polymerization, the r_1r_2 values would suggest that the insolubles fraction was comprised of polymer chains with slightly blocky character.

Turning to the compositional analysis of the parent resins, the results show that the mol% 1-hexene for all the parent resins is around 4%. Values of r_1r_2 for the parent resins range between 1.29 and 3.0, all greater than one and all indicating a propensity toward blockiness. The RMD values range from 91 to 98%, all under 100% and again suggesting a blocky character to the polymerization. Based on the parent resins, one would conclude that these Ziegler–Natta polymerizations have a blocky character, and are non-random. On a chain level basis, this is clearly in conflict with the analyses of the fractions.

Since we have the composition of the fractions, and the amount of each fraction, the composition of the parents can be derived mathematically. The approach taken was to determine the 'mole' percent of each fraction using the appropriate average monomer equivalent weight. Thus for a 20 mol% copolymer, the average monomer equivalent weight would be $0.2M_\mathrm{w}$(1-hexene) $+ 0.8M_\mathrm{w}$(ethylene). The estimated mol% of each monomer, dyad, and triads in the parent can be obtained from the weighted averages using the derived mol% of each fraction and the compositional values for the fractions. The values for r_1r_2 and RMD were then obtained from the calculated compositional values. While it should be obvious, the values of r_1r_2 and RMD are not amenable to direct mathematical combination.

The compositional and dispersity results obtained mathematically agree very well with the results observed directly. This not only validates the mathematical approach, but also demonstrates that the decrease in relative monomer dispersities (and the increase in reactivity ratio products) for the parents, as compared to the fractions, results from simple mixing rules. That is, resin composed of a compositionally heterogeneous mixture of polymer chains, all having a random or even alternating character, will appear to show *blockiness* character. In reality, none of the polymerizations produced blocked copolymers.

Looking at these conclusions in another light, the observation of a blocky character for ethylene polymerizations is consistent with the presence of several different types of chains, each with varying amounts of comonomer (chain comonomer heterogeneity). It is clear that some chains are produced with high comonomer content (solubles) and other chains are produced with low comonomer content (insolubles). The ensemble polymerization has a 'blocky' character, e.g. there is a non-random (and blocky) distribution of comonomer among the various chains. However, these results clearly cannot be considered to be a product of a single or even multiple catalyst sites producing individual chains with a blocky character.

The inadvisability of over interpreting the RMD or product of reactivity ratios parameters for resins from heterogeneous polymerizations is obvious. That is not to say that these parameters have no value, simply that they are influenced greatly by, and are primarily are measures of, resin heterogeneity. For instance, if the RMD for resin A was lower than the RMD for a resin B, it follows that resin A is more heterogeneous than resin B. Without fractionation, it is not possible to determine whether the heterogeneity ('blockiness') is within a single polymer chain ('blocked copolymerization') or founded in the mixture of resins with diverse comonomer content (‘chain comonomer heterogeneity’).

Kinetically, it is difficult to rationalize the former. To produce blocked copolymers, the reaction rate of the comonomer with an ethylene based propagation site (k_{12}) would have to be slower than the reaction rate with a comonomer based propagation site (k_{22}). In addition, the reaction rate of ethylene with a comonomer based propagation site (k_{21}) should be slower than the reaction rate with an ethylene based propagation site (k_{11}). While is generally accepted that the second condition is met, the rate of 1-hexene reacting with a comonomer based propagation site (k_{22}) is believed to be slower than the rate of reaction with an ethylene based site (k_{12}) [16]. This later, in and of itself, would make formation of hexene/hexene blocks disfavored as long as ethylene was present.

The compositional analysis of the solubles fractions illustrates this point. The comonomer content strongly indicates that these chains were formed in an environment in which the ethylene/1-hexene ratio was low. Under these conditions, the probability for 1-hexene reacting with a 1-hexene based propagation site is high. Yet, even under these conditions, these fractions showed alternating polymerization character, e.g., there are less hexene/hexene dyads than expected based on simple Bernoulian statistics ($k_{22} < k_{12}$).

The reaction rate of 1-hexene versus ethylene is further illustrated by considering the molar ratios of the products and the molar ratios found in the reactor (Table 2). The molar ratio experienced at the polymerization sites will be close to that observed in the flash gas analysis, obtained by analyzing a liquid portion of the reactor contents during polymerization. In all cases, the ethylene/1-hexene molar ratio observed for the products is higher than the flash gas analyses, which can only occur if ethylene polymerizes faster than 1-hexene ($k_{11} > k_{12}$ and $k_{21} > k_{22}$).

These data and relative kinetics clearly support the conclusion that the blockiness observed in analyzing polyethylene copolymers is not from the classically defined blocked polymerization, but rather chain comonomer heterogeneity. This heterogeneity may arise from catalyst heterogeneity or heterogeneity of the polymerization itself. The consequences of catalyst heterogeneity are clear, e.g., different catalyst sites produce ethylene copolymers with different comonomer content. In these examples, the two fractions are comprised of polymer chains that vary significantly in the comonomer content. The character of the polymerizations (alternating to random) supports the presence of two distinctly different catalyst sites, since each catalyst site will produce chains that posses this character as long as ethylene reacts faster than 1-hexene. As an aside, extending the mathematics of mixing to the insolubles fraction would support the assertion that the insoluble fraction is also comprised of chains produced from several additional different catalyst sites, each with unique comonomer content, though less diverse.

Table 2
Ethylene/1-hexene molar ratios for Ziegler–Natta resins and fractions

	Fractions				
	Solubles	Insolubles	Parent	Feed	Flash gas
Resin 250A	4.8	37.5	26.2	7.1	1.1
Resin 251	4.6	42.5	26.8	6.4	0.3
Resin 270B	4.2	39	24	7.1	1.1

The consequences of polymerization heterogeneity cannot be easily separated from those of catalyst heterogeneity. Each chain is produced from a unique set of polymerization conditions, one of which is the catalyst site. Other conditions include temperature, pressure, and ethylene/1-hexene ratio. As the slurry polymerization proceeds, the polymer particle grows in size [17]. More importantly, the polymerization occurs at the center of the growing polymer particle [18,19]. The non-polar nature of polymer particles coupled with diffusion, temperature gradients, etc., clearly allows the conditions experienced by the catalyst site to change with time. If there are any step changes, subsequent fractionation and characterization could easily confuse this step change in conditions with the presence of multiple catalyst sites, each with their own comonomer incorporation efficiency and propagation/termination rates.

4. Conclusions

In general, for any polymerization system where there is the possibility for compositional heterogeneity, the RMD and the reactivity ratio products are influenced by this heterogeneity. The values obtained for a heterogeneous polymer mixture will suggest a less random polymerization than actually occurs at the microstructural level. To determine the compositional properties for a resin produced from a heterogeneous polymerization, a separation step is required prior to the determination of randomness. For the catalyst system studied in this paper, compositional analysis not only confirms the heterogeneity of the resin, but also suggests there are at least two catalyst sites.

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