

Customizing the comonomer incorporation distribution in Ziegler–Natta-based LLDPE: Harnessing the influences of the titanation temperature during catalyst synthesis and of polymerization process parameters

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Abstract

The microstructure of linear low-density polyethylene (LLDPE) is strongly influenced by short-chain branches (SCBs) incorporated into the polymer backbone. Varying the number, distribution, and length of SCBs allows the properties of the resulting polymer to be tailored to meet specific requirements. Using Ziegler–Natta (ZN) catalysts for synthesis has disadvantages in terms of the comonomer incorporation distribution (CID) compared to, for instance, metallocene and post-metallocene catalysts. Nevertheless, ZN catalysts continue to be widely used, as many of the new generations of catalysts are more difficult to handle and cannot match the cheap cost of ZN catalysts. To improve this aspect of ZN catalysts, we investigated the influence of catalyst titanation temperature and polymerization process parameters on the CID. Our results show that it is possible to manipulate the process parameters of the present ZN catalyst system to yield a desired comonomer amount and CID in the polymer. Varying the titanation temperature clearly influenced the titanium content of the catalyst. Molecular-weight distribution analysis and deconvolution results indicate that changes in the amounts of comonomer incorporated and in the CID are directly related to the catalyst's active site that produces the lowest-molecular-weight fraction.

KEYWORDS

chemical composition distribution (CCD), comonomer incorporation distribution, linear low-density polyethylene (LLDPE), titanation temperature, Ziegler–Natta catalysis

1 | INTRODUCTION

Polyolefins are ideal materials for many modern applications as they offer the desired properties at low

manufacturing costs. Ziegler–Natta (ZN) catalyst systems are of great importance in the production of linear low-density polyethylene (LLDPE) at low pressures.^[1–3] Use of comonomers introduces side

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chains along the backbone of the polymer and thus allows the resulting polymer properties to be influenced. As these side chains disrupt the typical lamellar structure of polyethylene, they have a direct effect on the crystallization speed and final crystallinity of the polymer. Frequency and length of the side chains allow the relative percentage of the amorphous fraction to be modified.^[4,5]

Compared to modern catalyst systems using, for instance, metallocene catalysts in LLDPE production, ZN catalysts exhibit some deficiencies in terms of the properties of the polymer produced. To ensure that the polymer is consistent in its properties across the entire molecular weight distribution (MWD), the amount of comonomer incorporated should be uniformly distributed.^[4] Typical ZN catalysts, however, do not achieve this uniformity: High amounts of comonomer are incorporated into the lower-molar-mass fractions, and with increasing overall molar mass, the amount of comonomer incorporated decreases significantly. This results in a polymer that varies in its properties. Comparison of LLDPE samples with uniform and with typical ZN incorporation distributions showed that, for the same amount of comonomer, the former exhibited lower crystallinity than the latter.^[1,4]

The chemical composition distribution (CCD) can be customized in several ways to mitigate the incorporation behaviour of the ZN catalyst. If the CCD is to be influenced directly during polymerization, multistage processes can be used to deliberately produce a uniform CCD determined by the reaction conditions in the individual reactors. Another option is to use several catalyst systems which—in combination—produce the desired CCD. If the CCD is to be influenced or corrected by post-polymerization, a variety of polymers can be blended to produce a uniform CCD. However, this method has significant disadvantages, as it is very energy-intensive and requires considerable effort to produce a well-mixed permanent blend.^[1,5]

Due to the multi-site nature of ZN catalyst systems, LLDPE samples usually exhibit a polydispersity index (PDI) between 4 and 20.^[6] In order to better describe this broad MWD, models are applied to assign individual molar-mass fractions to active sites, and the MWD is considered as a blend of several narrow molar-mass fractions.^[7,8] This inverse computational technique enables the prediction of the microstructure of the polymer, and the polymerization conditions can be adjusted accordingly. These models vary in complexity depending on whether mass and heat transfer resistance are considered. The MWD is deconvoluted into most probable Flory–Schultz distributions with associated comonomer content based on data from high-temperature size-exclusion chromatography (HT-SEC). Modelling of the comonomer content for the

corresponding active sites is based on the Stockmayer bivariate distribution. In general, using the Levenberg Marquardt minimization method, the MWD curves are fitted to 4–6 active centres until a minimum is found.^[9–11]

Building on these studies and on our previous work,^[12–14] we explored extensively the influence of the titration temperature during catalyst synthesis on the microstructure and the incorporation distribution of the comonomer in LLDPE samples (Figure 1). Varying the titration temperature over a broad range, we found that it is possible to synthesize catalysts that produce a more uniform comonomer incorporation distribution.

2 | EXPERIMENTAL SECTION

ZN catalyst was synthesized via the precipitation process in two stages following methods described in the literature.^[13,15–17] The catalyst samples produced differed in the titration temperature used during synthesis, while all other parameters were kept constant except for minor adjustments. The minor changes relate to the Mg/alcohol ratio (2/1 instead of 1.83), the stabilization time for the MgCl₂ which was increased from 0.5 to 1 h, hexane which was replaced by heptane as the washing agent, and the washing step which was performed at room temperature (20–21°C). The catalysts obtained were then studied in terms of polymerization behaviour under various process conditions in a 0.5 L bench-scale polymerization reactor.

2.1 | Catalyst synthesis

For MgCl₂ support material preparation, a 20.4% solution of butyloctyl-magnesium (8.55 mmol, in *n*-heptane, Lanxess) was placed in a Schlenk flask. Under vigorous stirring, 2-ethyl-hexanol (17.2 mmol, Sigma-Aldrich) was added at temperatures between 0 and 5°C. An ethyl aluminium-dichloride (EtAlCl₂) solution (25.3% in *n*-heptane, Lanxess) was placed in a separate Schlenk flask, to which the magnesium–alcoholate solution from the initial step was then slowly added dropwise at 60°C. After the precipitate had settled, the reaction mixture was separated by centrifugation and the slurry washed twice with 5 mL *n*-heptane (97%, Roth). In the second synthesis step, the carrier slurry described above was heated to the given titration temperature (T_{Ti}) under vigorous stirring. TiCl₄ (≈19% toluene, TCI) was added to this solution over a period of 30 min. After the complete addition of the TiCl₄, the reaction mixture was stirred at T_{Ti} for an additional 40 min. The catalyst obtained was separated by centrifugation and washed three times with about 2 mL

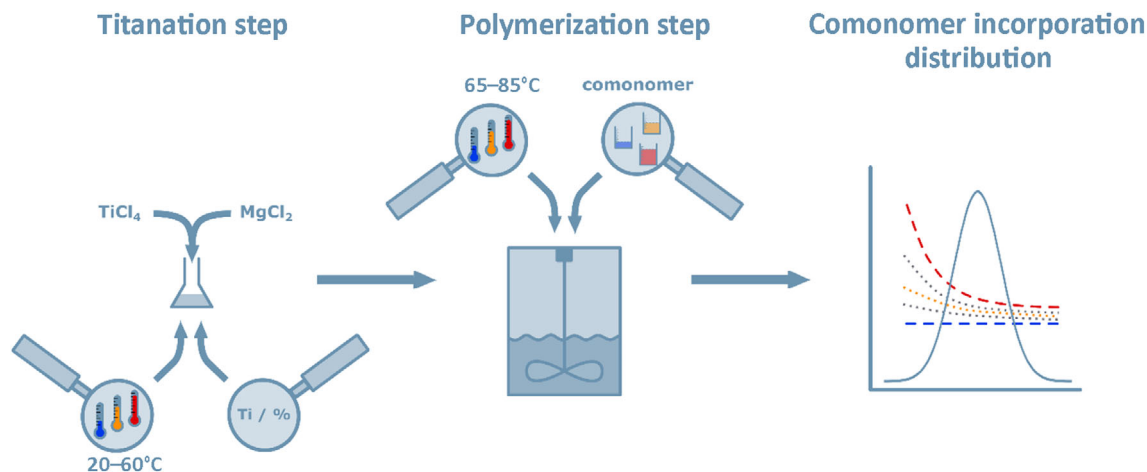


FIGURE 1 Schematic overview of the process steps investigated—titanation temperature during catalyst synthesis and the process parameters during polymerization—to determine their influences on comonomer incorporation distribution in Ziegler–Natta (ZN) catalyst systems.

of *n*-heptane at room temperature. In the last step, the catalyst was vacuum-dried at room temperature and then stored in a glovebox.

2.2 | Polymerization setup

All gases and solvents used for polymerization were purified before introduction into the reactor system. The following chemicals were used for polymerization: ethylene (3.0, Linde), *n*-butene (2.5, Linde), propane (3.5, Gerling Holz Co), nitrogen (5.0, Linde), hydrogen (5.0, Linde), and *n*-heptane (97%, Roth). The operating principle of the purification unit has been described in detail elsewhere.^[18,19]

Triethyl-aluminium (TEA) (93%, Sigma Aldrich) was used as a cocatalyst. For the polymerization experiments, catalyst and cocatalyst were stored and prepared in a glovebox (Braun) under inert conditions (N_2 , < 1 ppm O_2 , < 1 ppm H_2O). Both catalyst and cocatalyst were suspended in paraffin oil (Shell Ondina 933) before injection into the reactor system. In all polymerization experiments, an Al/Ti ratio of 100 was used.

A detailed description of the reactor setup can be found in previous publications.^[9,20] In order to minimize possible contaminant interference, the reactor was cleaned before each experiment using three cycles of nitrogen purging followed by evacuation of the reactor. To remove remaining traces of moisture, 80 g propane were filled into the reactor, which was then heated to >90°C for at least 30 min to ensure that the impurities can be purged with the propane at the end of the purification process.

For the main polymerization, 160 g propane, 8 g ethylene, the intended amount of *n*-butene, and 50 mg

hydrogen were fed into the reactor. The initial amount of ethylene was intended to ensure that sufficient monomer was already present during the heating process if polymerization started before the polymerization temperature was reached. The reactor pressure during polymerization was determined on the basis of preliminary tests. For this purpose, propane, hydrogen, ethylene (initial amount 8 g), and comonomer were supplied to the reactor, and the reaction mixture was heated up to the individual polymerization temperatures (no addition of catalyst/cocatalyst during the preliminary experiments). The resulting pressure was used as set point for the ethylene mass flow controller during the following experiments at the corresponding process conditions. Both 3 mg (supported) catalyst and the required amount cocatalyst were injected into the reactor after 10 min of pre-contacting time at 30°C. After injection, the reactor was heated from 30°C to the designated reaction temperature. As soon as a constant temperature had been reached, polymerization was performed for 30 min. The slurry reaction mixture was stirred by a propeller stirrer at 400 rpm. Ethylene uptake and polymer yield were used to derive the catalyst activity curve and to calculate the polymerization activity rate (R_p).

2.3 | High-temperature size-exclusion chromatography (HT-SEC)

The key molecular properties of the polymers were determined by HT-SEC analysis, which provided information on average molar mass M_w , number average M_n , dispersity index D , and comonomer content. The device used was an HT-SEC with an IR5 detector from PolymerChar

with three PLgel Olexis mixed-bed columns (300 mm length) from Agilent.

1,2,4-trichlorobenzene (TCB) at 160°C was used as a solvent, and the polymer samples were dissolved at 160°C for 90 min under continuous shaking. Prior to use, the TCB was distilled, filtered, and stabilized with butylhydroxytoluene.

Based on the short-chain branches per 1000 total carbons (SCB/1000TC), the comonomer content was calculated according to the following:

$$w_{\text{comonomer}} = \frac{\text{SCB}/1000\text{TC} \cdot M_{\text{comonomer}}}{500 \cdot M_{\text{C}_2\text{H}_4}} \cdot 100 \quad (1)$$

$w_{\text{comonomer}}$... comonomer content/mass%; SCB/1000TC ... short chain branches per 1000 total carbons; $M_{\text{comonomer}}$... molar mass of the comonomer/g mol⁻¹; and $M_{\text{C}_2\text{H}_4}$... molar mass of ethylene/g mol⁻¹.

2.4 | Differential scanning calorimetry (DSC)

A DSC3+ from Mettler Toledo was used for measurement. The samples were analyzed at a heating/cooling rate of 10°C min⁻¹ between 40 and 180°C in an N₂ atmosphere. To prepare each sample, about 3 mg of polymer powder was weighed into an aluminium crucible. Two heating cycles were performed for each sample, and the second heating curve was used for evaluation. Crystallinity was calculated based on the melting enthalpies obtained, using the theoretical value of 293 J g⁻¹ for completely crystalline polyethylene.^[21]

2.5 | Inductively coupled plasma mass spectroscopy (ICP-MS)

To determine the titanium content of the ZN catalyst, ≈100 mg of the catalyst was treated by microwave digestion at 180°C for 20 min using an acid mixture consisting of 3.5 mL HNO₃, 1.5 mL HCl, and 3 mL HF in a CEM Mars 6 microwave digestion unit. Before measurement, 200 μL solutions were diluted with ultra-pure water (18 MOhm) containing 1% HNO₃ and 0.5% HF to 50 mL. To determine aluminium and magnesium content, 10 mL of HNO₃ was used and treated with the same digestion program, and for dilution, ultra-pure water containing 1% HNO₃ was used. The solution was then analyzed using a Thermo Scientific XSERIES 2 ICP-MS; calibration was performed using 1–1000 ppb of the ICP-MS-68B-B mixed-element standard from high purity standards.

3 | RESULTS AND DISCUSSION

3.1 | Influencing process parameters

Previous studies have investigated the influence of the titanation temperature (T_{Ti}) during catalyst synthesis on the CID in LLDPE. In a study by Aigner et al.,^[12] it was shown for a small set of parameters that a low titanation temperature favours uniform comonomer incorporation. In a previous study by our group,^[14] this investigation was extended to include a wide range of process parameters of the polymerization step. The present study aimed at further increasing our understanding by studying a wide range of titanation temperatures during catalyst synthesis. We sought to determine the ideal titanation temperature for achieving the most uniform CID at given process parameters.

The two studies mentioned above^[12,14] investigated the influences on the CID of broad ranges of three polymerization process parameters—comonomer type, comonomer quantity used, and polymerization temperature. The process parameters for the present study were selected based on these findings, but the role of comonomer type was not investigated (see Section 3.3). As previously published, CID uniformity decreases with increasing length of the comonomer chain, which was also assumed for the catalysts investigated in this study. Since this is in agreement with the literature,^[22,23] this was also assumed for the catalysts investigated in this study.

We thus investigated the influencing factors given in Table 1, where variation of the titanation temperature relates to the catalyst synthesis step, and variations of the polymerization temperature and of the amount of *n*-butene relate to the process conditions for the polymerization experiments.

To ensure reproducibility of the results obtained for the process parameters, preliminary experiments were carried out, which served as a basis for calculating the error tolerances. The results (see Table 2) were applied to all analysis methods described in the following sections.

TABLE 1 Process parameters used to study comonomer incorporation behaviour in linear low-density polyethylene (LLDPE).

| Titanation temperature (°C) | 20 ^a , 30, 40, 50, 60, |
|---------------------------------|---------------------------------------|
| Comonomer type | <i>n</i> -butene |
| Comonomer quantity used (mmol) | 35.6 (low), 101.5 (mid), 178.2 (high) |
| Polymerization temperature (°C) | 65, 75, 85 |

^a... 20°C corresponding to room temperature.

TABLE 2 Preliminary tests were done with *n*-butene (35.6 mmol) at a polymerization temperature of 75°C based on the catalyst system obtained at $T_{Ti} = 20^\circ\text{C}$ with a titanium content of 5.78%.

| Entry | M_w (g mol ⁻¹) | M_n (g Mol ⁻¹) | PDI | R_p (kg _{Poly} g _{cat} ⁻¹ h ⁻¹) | Comonomer (mol%) |
|-------|------------------------------|------------------------------|------|--|------------------|
| 1 | 119,800 | 19,200 | 6.24 | 13.8 | 0.92 |
| 2 | 122,000 | 21,300 | 5.72 | 13.1 | 0.72 |
| 3 | 137,500 | 25,400 | 5.42 | 8.9 | 0.76 |

Abbreviation: PDI, polydispersity index.

TABLE 3 Inductively coupled plasma mass spectroscopy (ICP-MS) analysis of the Ziegler–Natta (ZN) catalysts synthesized at various titanation temperatures.

| Catalyst | T_{Ti} (°C) | Ti (wt.%) | Mg (wt.%) | Al (wt.%) |
|----------|-----------------|-----------|-----------|-----------|
| 1 | 20 ^a | 5.78 | 12.61 | 1.94 |
| 2 | 30 | 5.82 | 12.68 | 1.74 |
| 3 | 40 | 6.73 | 14.22 | 1.45 |
| 4 | 50 | 6.87 | 10.92 | 1.15 |
| 5 | 60 | 9.11 | 11.53 | 1.77 |

^a... 20°C corresponding to room temperature.

3.2 | Titanation temperature T_{Ti}

Previous studies have demonstrated the influence of the titanation temperature during catalyst synthesis on the incorporation behaviour of the comonomer during polymerization. Usually, titanation temperatures greater than 60°C are used in the precipitation process of ZN catalyst synthesis,^[24] but little data is available on the effects of lower titanation temperatures. Initial studies of catalysts synthesized at a titanation temperature of 40°C demonstrated an improvement in comonomer incorporation behaviour.^[12,14] The titanation temperature also influences the absolute amount of comonomer incorporated.

We varied the titanation temperature between 20 and 60°C to determine (i) whether titanation takes place as desired and (ii) the extent to which the titanation temperature within this range influences the absolute amount of titanium taken up by the catalyst system. Table 3 shows the experimental parameters and analytical data for the catalysts synthesized. Clearly, the titanium content increased with increasing titanation temperature. Even at room temperature, more than 5% titanium was incorporated into the substrate, which is considered sufficient in terms of ZN catalyst titanium loading.

Since the remaining steps of catalyst synthesis remained unchanged, the differences in the results can clearly be attributed to the influence of the titanation temperature. Slight variations in colour due to differences in the ratio of

the oxidation states of the titanium atom were visible during synthesis, but these were not investigated further.

3.3 | Impact of titanation temperature on molecular properties

It is commonly accepted that the polymerization activity in ZN-catalyzed polymerization processes increases with increasing polymerization temperature. We investigated the extent to which this is affected by the titanation temperature, as summarized for the general molecular properties in Table 4: There was a slight trend towards lower polymerization activity with increasing titanation temperature; this trend is not statistically significant and fluctuations are to be expected, especially when the polymerization activity is evaluated.

These variations resulted from the considerable differences in titanium content of the catalysts, as higher titanium content in the catalyst enhances the polymerization process. Since, for reasons of comparability, the polymerization conditions were not adjusted to the process parameters, it was much more difficult—especially in the first few minutes of polymerization—to keep the experiments with high-titanium-content catalysts in equilibrium and to establish constant temperature and ethylene pressure ratios than in experiments with low-titanium-content catalysts. However, the results show that the polymerization activity was not significantly affected by varying the titanation temperature during catalyst preparation.

Our rationale for not comparing different comonomers in our experiments was this: An increase in polymerization temperature has an impact not only on the polymerization activity, but also on the comonomer incorporation behaviour. The rate of comonomer incorporation increases with increasing polymerization temperature and with decreasing length of the comonomer. Due to decreasing incorporation efficiency with increasing chain length of the comonomer, the amount of liquid comonomer present in the reactor system increases, which shifts the solvent equilibrium. This would have added another influencing factor to be considered in

TABLE 4 Results of high-temperature size-exclusion chromatography (HT-SEC) and differential scanning calorimetry (DSC) analyses and of polymerization activity-rate calculation.

| T_{Ti} (°C) | $n_{comonomer}$ (mmol) | T (°C) | M_w (g mol ⁻¹) | M_n (g mol ⁻¹) | PDI | Comonomer (mass%) | Crystallinity (%) | R_p (kg _{Poly} g _{cat} ⁻¹ h ⁻¹) | R_p (kg _{Poly} g _{Ti} ⁻¹ h ⁻¹) |
|---------------|------------------------|----------|------------------------------|------------------------------|------|-------------------|-------------------|--|---|
| 20 | 35.6 | 65 | 156,900 | 28,400 | 5.52 | 0.8 | 64.2 | 10.9 | 189.3 |
| | | 75 | 104,600 | 20,300 | 5.16 | 3.4 | 48.6 | 11.5 | 198.4 |
| | | 85 | 101,400 | 19,500 | 5.20 | 5.6 | 42.2 | 12.5 | 216.7 |
| | 101.5 | 65 | 141,000 | 23,200 | 6.08 | 0.8 | 62.0 | 12.4 | 214.6 |
| | | 75 | 121,300 | 22,600 | 5.36 | 3.0 | 50.5 | 10.4 | 180.7 |
| | | 85 | 119,600 | 20,900 | 5.73 | 5.7 | 40.0 | 10.1 | 175.3 |
| | 178.2 | 65 | 144,600 | 27,900 | 5.19 | 0.8 | 58.9 | 9.0 | 156.3 |
| | | 75 | 124,000 | 22,900 | 5.42 | 3.2 | 47.7 | 11.8 | 204.1 |
| | | 85 | 112,100 | 18,300 | 6.13 | 8.3 | 35.0 | 8.4 | 145.4 |
| 30 | 35.6 | 65 | 156,200 | 27,200 | 5.73 | 0.7 | 59.1 | 7.6 | 130.9 |
| | | 75 | 123,500 | 22,300 | 5.55 | 3.0 | 48.3 | 7.2 | 123.3 |
| | | 85 | 107,500 | 20,000 | 5.39 | 4.6 | 43.6 | 9.6 | 164.9 |
| | 101.5 | 65 | 131,100 | 21,300 | 6.16 | 1.2 | 56.2 | 13.4 | 230.3 |
| | | 75 | 127,100 | 21,800 | 5.83 | 3.0 | 50.3 | 11.1 | 190.9 |
| | | 85 | 104,700 | 17,900 | 5.85 | 6.1 | 40.0 | 8.6 | 147.3 |
| | 178.2 | 65 | 118,300 | 20,900 | 5.65 | 1.4 | 59.0 | 14.7 | 253.2 |
| | | 75 | 93,000 | 13,700 | 6.80 | 9.2 | 37.7 | 6.9 | 118.7 |
| | | 85 | 91,500 | 16,000 | 5.72 | 8.3 | 38.8 | 13.1 | 224.3 |
| 40 | 35.6 | 65 | 205,800 | 31,900 | 6.45 | 0.5 | 58.3 | 6.2 | 92.3 |
| | | 75 | 149,000 | 23,700 | 6.29 | 3.0 | 46.0 | 9.2 | 136.0 |
| | | 85 | 102,600 | 18,300 | 5.61 | 5.4 | 41.1 | 11.9 | 177.3 |
| | 101.5 | 65 | 219,000 | 29,200 | 7.50 | 0.9 | 55.1 | 7.1 | 105.1 |
| | | 75 | 86,300 | 13,900 | 6.19 | 6.2 | 38.9 | 13.6 | 202.3 |
| | | 85 | 89,900 | 15,600 | 5.75 | 6.8 | 39.1 | 12.5 | 185.6 |
| | 178.2 | 65 | 118,800 | 19,400 | 6.13 | 1.3 | 58.3 | 11.8 | 175.9 |
| | | 75 | 89,200 | 14,200 | 6.31 | 7.0 | 40.2 | 10.7 | 159.5 |
| | | 85 | 91,800 | 15,900 | 5.77 | 7.0 | 38.3 | 10.6 | 157.4 |
| 50 | 35.6 | 65 | 160,100 | 30,200 | 5.31 | 0.7 | 58.3 | 9.6 | 139.4 |
| | | 75 | 110,000 | 21,500 | 5.12 | 3.2 | 47.7 | 11.2 | 163.0 |
| | | 85 | 115,400 | 22,100 | 5.23 | 5.3 | 38.8 | 11.2 | 163.1 |
| | 101.5 | 65 | 152,100 | 27,900 | 5.45 | 0.6 | 60.4 | 11.5 | 166.8 |
| | | 75 | 124,700 | 25,400 | 4.91 | 2.2 | 51.5 | 11.7 | 170.7 |
| | | 85 | 118,900 | 21,900 | 5.42 | 4.7 | 41.3 | 11.2 | 163.4 |
| | 178.2 | 65 | 144,000 | 25,900 | 5.55 | 1.1 | 57.3 | 11.3 | 164.0 |
| | | 75 | 118,600 | 22,000 | 5.40 | 3.6 | 46.7 | 14.6 | 213.1 |
| | | 85 | 84,100 | 12,600 | 6.67 | 13.6 | 43.3 | 9.2 | 134.0 |
| 60 | 35.6 | 65 | 194,700 | 30,800 | 6.32 | 0.5 | 59.3 | 12.6 | 138.7 |
| | | 75 | 127,500 | 23,400 | 5.45 | 3.0 | 45.3 | 13.0 | 142.7 |
| | | 85 | 111,500 | 20,900 | 5.33 | 5.2 | 40.0 | 15.2 | 167.3 |
| | 101.5 | 65 | 143,400 | 25,500 | 5.63 | 0.7 | 59.7 | 16.2 | 177.4 |
| | | 75 | 109,400 | 18,700 | 5.85 | 3.9 | 41.3 | 18.1 | 199.2 |
| | | 85 | 93,200 | 15,900 | 5.87 | 8.8 | 34.7 | 11.0 | 120.7 |

TABLE 4 (Continued)

| T_{Ti} (°C) | $n_{comonomer}$ (mmol) | T (°C) | M_w (g mol ⁻¹) | M_n (g mol ⁻¹) | PDI | Comonomer (mass%) | Crystallinity (%) | R_p (kgPoly g _{cat} ⁻¹ h ⁻¹) | R_p (kgPoly g _{Ti} ⁻¹ h ⁻¹) |
|---------------|------------------------|----------|------------------------------|------------------------------|------|-------------------|-------------------|--|---|
| | 178.2 | 65 | 135,200 | 26,400 | 5.11 | 0.6 | 60.7 | 14.3 | 156.6 |
| | | 75 | 113,600 | 21,900 | 5.19 | 3.6 | 45.7 | 15.9 | 174.8 |
| | | 85 | 110,900 | 18,000 | 6.15 | 7.8 | 35.3 | 13.0 | 142.3 |

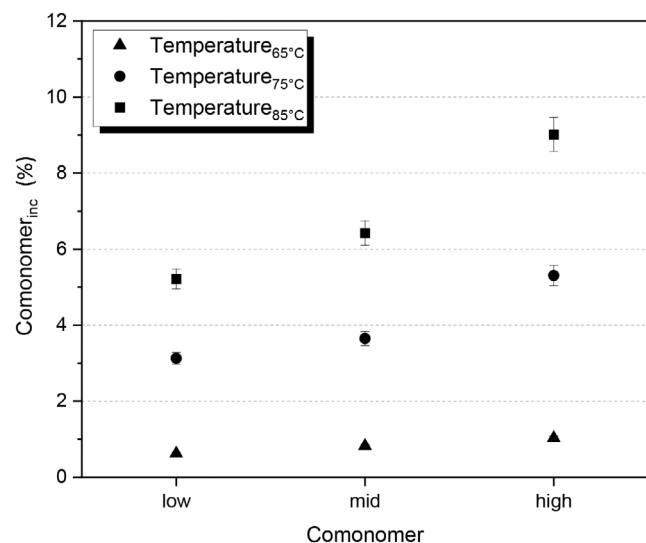


FIGURE 2 Comonomer incorporation as a function of polymerization temperature for various amounts of comonomer supplied. Matching polymerization process parameter sets of the different catalysts are combined for improved visualization.

process control and would have interfered with comparability to the *n*-butene experiments. We therefore decided to focus our experiments on *n*-butene incorporation only.

Figure 2 combines all data of all catalysts under the same process conditions and illustrates the influences of the amount of comonomer and the polymerization temperature on comonomer incorporation: Comonomer incorporation increased with increasing polymerization temperature and with increasing amount of comonomer supplied. Comparison of the results for individual catalysts produced at different titanation temperatures shows no significant trends (Table 4). Thus, the titanation temperature had no significant effect on the results, and for the catalysts investigated, we can predict the process conditions required to achieve specific product properties.

As previously stated,^[14] incorporation of the comonomer as a function of M_w is an important parameter that influences the properties of the product. For comparability reasons, a linear fit for the dependence of the comonomer content on the molecular weight was calculated for all comonomer curves, and the slope of the linear fit was used as a measure of the uniformity of the CID. If the CID is

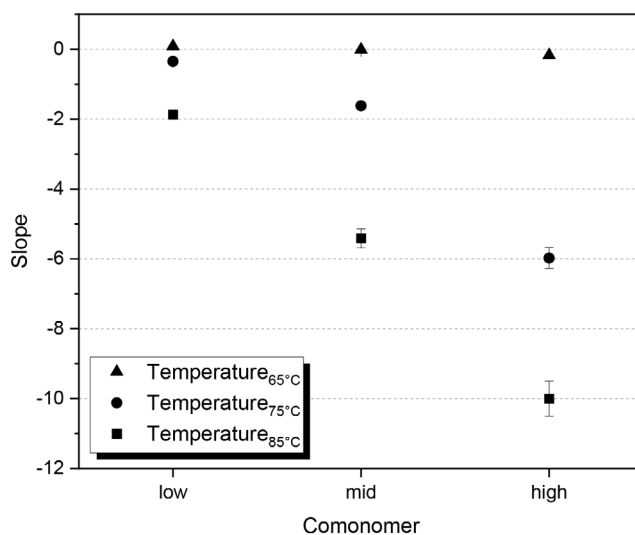


FIGURE 3 Slope of the comonomer content versus molecular weight as a function of the polymerization temperature for various amounts of comonomer supplied in the polymerization experiment. Matching polymerization process parameter sets of the different catalysts were combined for improved visualization. Slope data calculation has been explained in detail in a previous publication.^[14]

uniform, the slope of the linear fit tends to zero; the less uniform the comonomer incorporation, the further the values of the slope of the linear fit shift into the negative range. Evaluation of the incorporation distribution shows that specific selection of the process parameters allows tailoring of the product properties to given requirements. If, as for the incorporation rate, the data points are combined and given process conditions for all catalysts which are compared, it can be seen that increasing the amount of comonomer and the polymerization temperature causes a shift to less uniform comonomer incorporation. Conversely, a uniform incorporation distribution can be achieved if at least one of these two factors is kept low, as shown in Figure 3.

These two observations show that it is possible to create a library for customizing the polymer properties. Additionally, when taking the process conditions into account, it becomes possible to determine which of the two influencing factors—polymerization temperature or comonomer quantity—must be adapted in order to generate a specified comonomer content and incorporation distribution in the polymer.

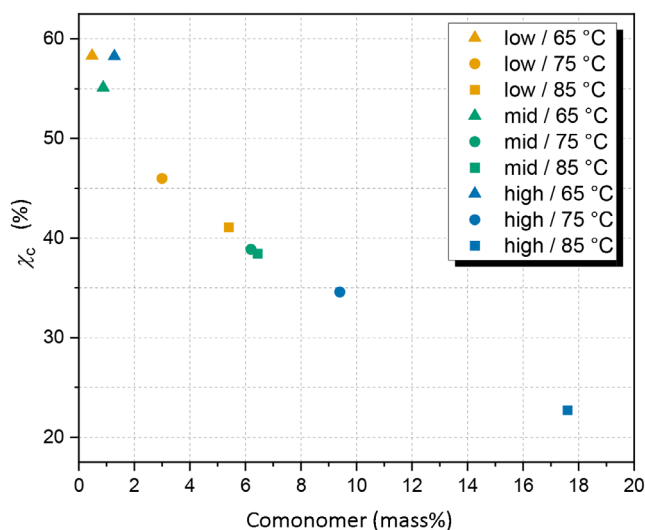


FIGURE 4 Crystallinity as a function of the *n*-butene content for polymers obtained with the catalyst made at a T_{Ti} of 40°C .

3.4 | Crystallinity

The results of the DSC analysis are consistent with the results of the SEC analysis. As can be seen in Table 4 and Figure 4, the crystallinity ranges were as expected. These were influenced both by the initial amount of comonomer and the polymerization temperature. All samples made at a polymerization temperature of 65°C exhibited a crystallinity of about 60%. Increasing the polymerization temperature and the initial amount of comonomer to the corresponding *mid* and *high* process conditions resulted in significantly lower crystallinity. As shown for the example of catalyst synthesized at $T_{Ti} = 40^\circ\text{C}$ in Figure 4, the results for low and medium comonomer amounts follow the same linear correlation between comonomer content and crystallinity. This behaviour was observed for all five catalysts synthesized.

Comparison of the results of the catalysts synthesized at different T_{Ti} showed only minor discrepancies, as can be seen in Figure 5: Crystallinities were consistently within the same range for all catalysts, which matches the results of the SEC analysis.

3.5 | Deconvolution analysis

For a more detailed evaluation of the molecular properties of the samples, MWD deconvolution and CCD were investigated by HT-SEC analysis. Note that HT-SEC analysis can only give the general MWD and does not provide detailed information on individual fractions, which would require more advanced fractionation technologies such as

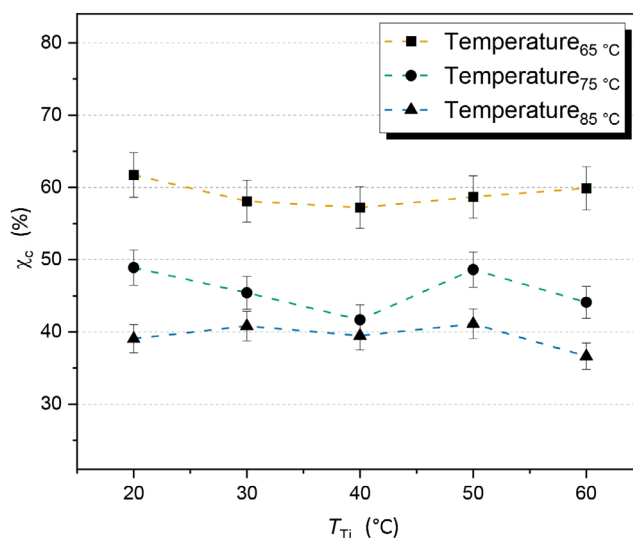


FIGURE 5 Crystallinities of the *n*-butene copolymers produced with catalysts synthesized at various titanation temperatures, where *high*, *mid*, and *low* indicate the amount of comonomer supplied during polymerization. Matching polymerization process parameter sets of the different catalysts were combined for improved visualization.

temperature rising elution fractionation (TREF) and crystallization analysis fractionation (CRYSTAF).^[25–27]

Deconvolution evaluation allows molecular properties to be assigned to specific fractions of the MWD. In addition to gaining more in-depth insights into the fractions of individual active sites, the comonomer content can also be assigned to individual active sites. This is of particular interest if the behaviour of non-uniform incorporation of the comonomer across the MWD is to be studied and influenced. Since this method is based on a mathematical model, it may give physically impossible results, especially in the lower boundary regions: If the comonomer content determined in the HT-SEC analysis is very low, the model outputs negative values for the comonomer content of the active centre of the lowest-molecular-weight fraction. These values were set to zero for further evaluation, since a negative comonomer content does not constitute a meaningful result.

ZN catalysts differ considerably from single site catalyst systems in terms of the uniformity of the polymer product produced. ZN catalysts exhibit high incorporation rates for comonomer in the low-molar-mass fractions, and with increasing molar mass comonomer incorporation decreases. This results in a polymer that varies in its molecular properties, since low-molar-mass fractions—with their high comonomer content—have properties that differ significantly from those of high-molar-mass fractions with much lower levels of comonomer.

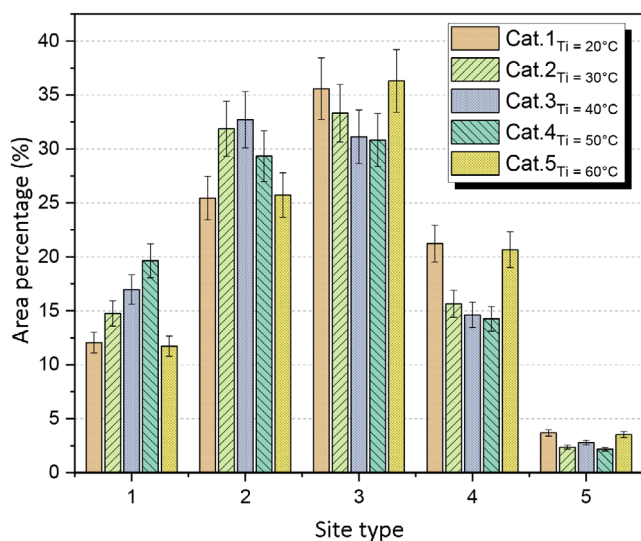


FIGURE 6 Area percentage results for the five deconvoluted active sites of our Ziegler–Natta (ZN) catalysts. With all catalysts, the polymerization experiments were performed at a polymerization temperature of 85°C, using a high amount of comonomer (178.2 mmol).

Assigning the comonomer content to the corresponding molar-mass fractions based on MWD deconvolution allows the influence of titination temperature on comonomer incorporation for low-molar-mass fractions to be studied. In this context, the catalysts can be compared and, as described above, a library of process parameters can be developed to achieve specified product properties for a given catalysts.

In the first step, the deconvolution analysis was performed for all data points to determine the minimum number of active sites by which the obtained SEC curve can be described with sufficient accuracy. This shows that all samples can be accurately described by five active sites. For further analysis, the SEC data obtained for each catalyst are evaluated using fixed M_n values. These are derived from the deconvolution of the centre point of the process conditions of the corresponding catalysts. In the following, the resulting trends for particular active sites within the process conditions can be analyzed for individual catalysts or for all catalysts in a comparative way. As expected, the differences between the catalysts increased at the boundaries of the process parameters ranges, especially when high comonomer concentrations were used. Since the data showed that the influence of the amount of comonomer introduced is greater than that of the polymerization temperature, the results for the samples prepared at a polymerization temperature of 85°C and with the highest amount of comonomer are discussed below.

As can be seen in Figures 6 and 7, using different titination temperatures had a significant effect. Comparison

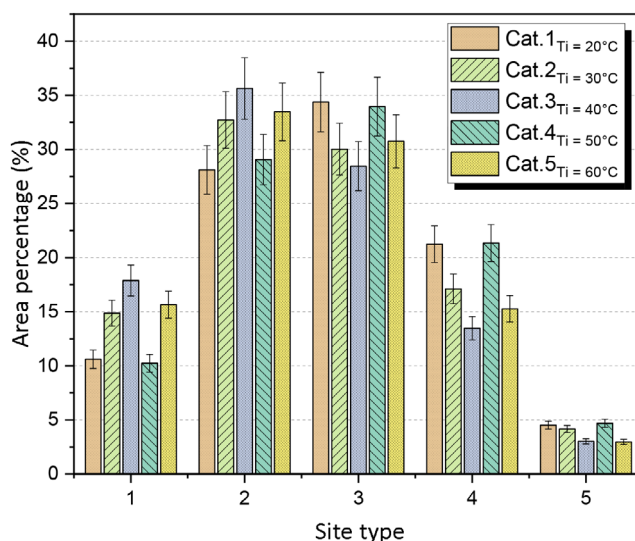


FIGURE 7 Area percentage results for the five deconvoluted active sites of our Ziegler–Natta (ZN) catalysts. With all catalysts, the polymerization experiments were performed at a polymerization temperature of 85°C, using a medium amount of comonomer (101.5 mmol).

of the catalysts produced at T_{Ti} between 20 and 60°C shows that higher area percentage values were obtained for the catalysts that had undergone titination at mid-range temperatures, especially for the first two centres with low average molar mass. For centres 4 and 5 in the high-molecular-weight region, the area percentage values were higher for the catalysts synthesized at 20 and 60°C titination temperature. The results for samples with lower comonomer content indicate that the interpretation of the data becomes more difficult and the results converge.

It can be seen (Figure 7) that only the first four active centres exhibit differences, which is why the influence of the titination temperature decreased in the range of high-molar-mass fractions. This is a further indication that the titination temperature is an interesting option for influencing the incorporation distribution of the comonomer especially in the low-molecular-weight region of the MWD.

We then studied the deconvolution results in terms of the amount of comonomer incorporated at each individual active site. The data confirm the typical incorporation behaviour for ZN catalysts, and particular attention has to be paid to the low-molecular-weight regions. As in the case of the area percentage results, the largest effects were found for the samples with the highest amount of comonomer (178.2 mmol) supplied. In Figure 8, it can be seen that the highest amount of comonomer was incorporated by the centre associated with the lowest-molar-mass fraction. The active centres with higher molar mass

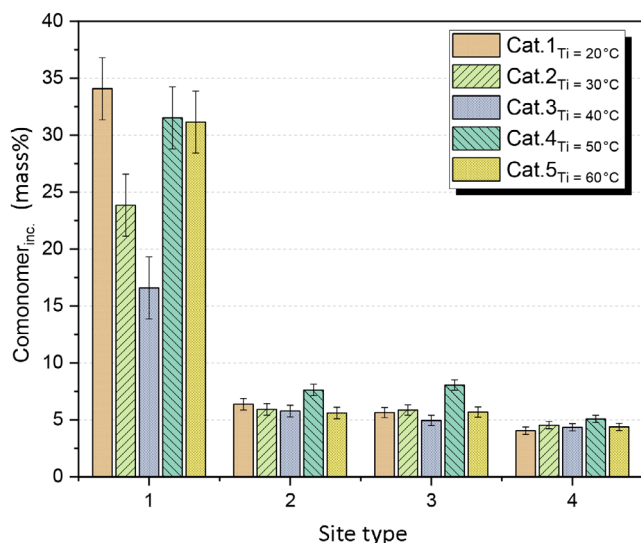


FIGURE 8 Comonomer content incorporated for the lowest four deconvoluted active sites of the Ziegler–Natta (ZN) catalysts. With all catalysts, the polymerization experiments were performed at a polymerization temperature of 85°C, using a high amount of comonomer (178.2 mmol).

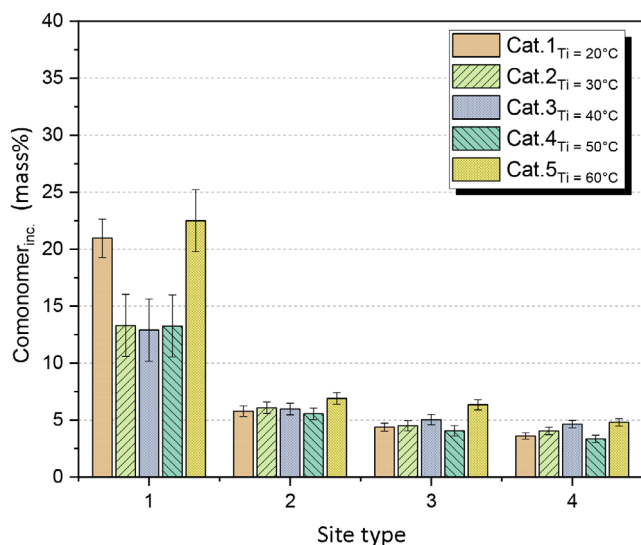


FIGURE 9 Comonomer content incorporated for the lowest four deconvoluted active sites of Ziegler–Natta (ZN) catalysts produced at a variety of titination temperatures (T_{Ti}). With all catalysts the polymerization experiments were performed at a polymerization temperature of 85°C, using a medium amount of comonomer (101.5 mmol).

incorporated significantly less comonomer; this applied to all catalysts and was also confirmed by samples with lower comonomer content, as shown in Figure 9. The most interesting finding in the comparison of the catalysts was made when only the active sites responsible for the lowest-molar-mass fraction were considered: The

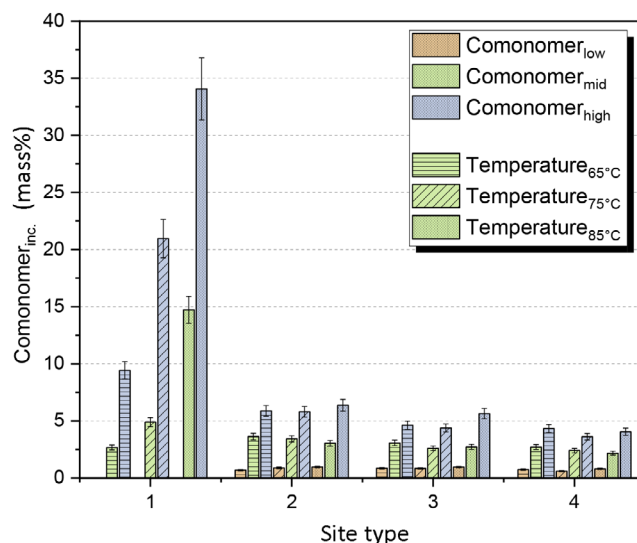


FIGURE 10 Comonomer content of all *n*-butene copolymers obtained by the catalyst made at $T_{Ti} = 20^\circ\text{C}$ calculated for each Flory–Schultz deconvoluted active site.

catalyst synthesized at $T_{Ti} = 40^\circ\text{C}$ showed the lowest incorporation rate, which means that the most uniform incorporation distribution over the entire MWD can be achieved with this catalyst because it exhibits the smallest difference between the first and second active centres. This is consistent with previous results.^[14]

The results of the comonomer content according to active centre for a given catalyst (and thus for a given titination temperature) were then analyzed (Figure 10). Again, for the active centres responsible for mid- and high-molecular-weight fractions, the incorporation rates were similar, and the process parameters had limited impact on the comonomer amount incorporated. The greatest differences were observed at the active site for the lowest-molecular-weight fraction, which showed the significant influence of the polymerization process parameters on the incorporation behaviour of the ZN catalyst. These deconvolution results suggest that the described library of process parameters affects mainly the properties of the active site of the lowest-molecular-weight fraction. If one of two process parameters—comonomer amount or polymerization temperature—is kept low, a uniform incorporation distribution of the comonomer can be obtained.

4 | CONCLUSION

Comparison of ZN catalysts prepared at titination temperatures in the range from 20 to 60°C demonstrated the influences of T_{Ti} on catalyst performance and on the properties of the LLDPE samples obtained. Varying the

titanation temperature during catalyst synthesis affected mainly the amount of titanium that can be introduced to the support material. However, reasonable titanation values were obtained over the entire range of 20–60°C.

Overall, analysis of the LLDPE samples showed that a toolbox of process parameters can be defined for these ZN catalysts to achieve specific polymer properties. If the focus is on a uniform incorporation distribution of the comonomer, the results from previous studies can be confirmed. If one of two process parameters—polymerization temperature or amount of comonomer provided—is kept low, a uniform incorporation distribution of the comonomer can be achieved.

The deconvolution results give a more detailed view of the molecular properties of the polymers and demonstrate that the titanation temperature influenced the comonomer content incorporated. Most notably, the active site of the lowest-molecular-weight fraction was most affected, and comparison of the catalysts showed that the catalyst produced at a titanation temperature of 40°C gave rise to the most uniform comonomer distribution.

A more in-depth analysis of the comonomer content of individual active centres found that the undesirable non-uniform incorporation behaviour of the ZN catalysts was limited to the active centre of the lowest-molar-mass fraction. The other active centres exhibited uniform incorporation behaviour, and the influence of the process parameters was negligible. Both variation of the titanation temperature during catalyst synthesis and process parameters during polymerization influence mainly the comonomer incorporation rate of the active site for the lowest-molecular-weight fraction.

AUTHOR CONTRIBUTIONS

Lukas Göpperl: Conceptualization; data curation; formal analysis; investigation; methodology; visualization; writing – original draft. **Daniel Christian Pernusch:** Software. **Julia Felicitas Schwarz:** Formal analysis. **Christian Paulik:** Project administration; resources; supervision; writing – review and editing.

PEER REVIEW

The peer review history for this article is available at <https://www.webofscience.com/api/gateway/wos/peer-review/10.1002/cjce.24896>.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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How to cite this article: L. Göpperl, D. C. Pernusch, J. F. Schwarz, C. Paulik, *Can. J. Chem. Eng.* **2023**, *1*. <https://doi.org/10.1002/cjce.24896>