

Describing and quantifying the chemical composition distribution in unimodal and multimodal ZN-polyethylene using CRYSTAF

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ABSTRACT: A new approach in describing and quantifying the chemical composition distribution (CCD) in Ziegler–Natta-polyethylene copolymers was developed by using crystallization analysis fractionation (Crystaf). Copolymers of ethylene and α -olefins (1-butene and 1-hexene) polymerized with different ZN catalyst systems were analyzed. Distinct differences in the CCD between the different polymer types (catalyst-cocatalyst system and comonomer type) were observed and could be quantified. Same approach was applied to 2-dimensional fractionation technique, cross fractionation chromatography, to describe and quantify the CCD of multimodal polyethylene copolymers. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43089.

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INTRODUCTION

Copolymers of ethylene and α -olefins synthesized with Ziegler–Natta (ZN) catalysts are heterogeneous in terms of molecular weight (M_w) and chemical composition (CC). The incorporation of short chain branches and their distribution along and across the polymer chains together with the molecular weight distribution define the end properties of the polyethylene products.

Beside this, the broadness of the molecular weight distribution (MWD) and chemical composition distribution (CCD) are highly influenced by the chemistry of the catalyst and the polymerization conditions. One important goal in the further development of ZN catalyst systems besides increasing the activity, tailoring the hydrogen and comonomer responses and improving morphology and plant operability, is to optimize/modify the catalyst formulations in the way that promotes and leads to desirable changes in MWD and CCD. Therefore it is crucial to be able to characterize the microstructures of ethylene and α -olefins copolymers in details. Polymer fractionation techniques enable the separation fractionation of polyolefins according to specific characteristics of their microstructures as defined by their distributions of molecular weight,^{1–5} chemical composition,^{6–10} tacticity,^{9,11} and long-chain branching,¹² resulting in gathering of significant information of the polymer structure. The most widely used technique to determine the MWD of polyolefins is high temperature gel permeation chromatography (HT-GPC),^{1–3} while the CCD characterization of PE can be done by Crystallization Analysis Fractionation (Crystaf),⁷ analytical—

Temperature Rising Elution Fractionation (a-TREF)^{6,7} and since recently also by Liquid Adsorption Chromatography (LAC).^{9,10}

The separation in Crystaf and TREF techniques is based on the fact that the crystallization temperature decreases with higher comonomer content in the polymer chain, where in LAC technique the separation is based on interaction between the stationary phase and the polymer in solution.

The CCD of ZN-ethylene and α -olefin copolymers is bimodal in terms of chemical composition holding a high crystalline homopolymer peak and a broader copolymer peak that contains significant comonomer content and therefore has lower crystallinity. The broadness of these peaks, beside the comonomer amount and type, also depends on the corresponding ZN catalyst used during polymerization.

To be able to further develop ZN catalyst systems it is crucial to have a tool to quantify the CCD in the polymer. Therefore, the information obtained from the Crystaf or TREF curves needs to be identified and quantified. A very simple and useful approach is to determine weight percentages of the soluble fraction and the homopolymer fraction in ethylene and α -olefins copolymers. One of the first approaches to describe the breadth of the CCD is done in a similar way as the M_n and M_w calculation from the GPC analysis by substituting the molecular weight with elution or crystallization temperatures where the correspondent T_n , T_w , and r parameters are obtained.⁷ By converting the elution temperatures to the SCB content using a calibration curve, number

average and weight averaged short chain SCB content can be calculated in a similar way as T_n and T_w .^{13,14} Zhang *et al.* concluded from their results that for these calculation approaches it should be considered that metallocene polyethylene copolymer sample had a higher SCB content and ZN sample showed a broader distribution which was evidenced by the respective ratio (C_w to C_n or T_w to T_n).^{12–14} The broadness of the CRYSTAF or TREF profile can also be defined by the difference of the elution temperature at which 25% (T_{25}) and the temperature at which 75% of the polymer elutes (T_{75}).¹⁵

In patent literature also other parameters are introduced to describe the CCD of linear low density polyethylene (LLDPE) using different calculation approaches.^{15–18} A Composition Distribution parameter (Cb) was defined by Watanabe *et al.*¹⁶ which is describing the breadth of the composition distribution obtained from p-TREF analysis and ¹³C-NMR of the obtained fractions.

The composition distribution breadth index (CDBI) describes the weight percent of copolymer molecules having comonomer content within 50% of the median total molar comonomer content.¹⁷ A similar approach is used by solubility distribution breadth index (SDBI) which gives the standard deviation of the CCD.¹⁸

These approaches, except CDBI, are not taking into account the effect of the comonomer content and type on the calculated indices.

This dependency is influenced by the fact that the peak shape depends on the comonomer amount and type.¹⁹ Even though CDBI is very strong in comparing the CCD of different unimodal and bimodal SS-LLDPE, it is not as good for comparison of CCDs of ZN-LLDPE copolymers, especially when the comonomer content is quite low leading to the large high density peak with the median at the high density peak. Thus, differences in the breadth of the copolymer fractions are not always sufficiently captured. Another shortage of these calculation approaches is that these are only usable to link the performance of the ZN catalyst systems in regards to the CCD of unimodal ethylene and α -olefins copolymers but not for ethylene and α -olefins copolymers having a bimodal MWD. Due to the fact that CRYSTAF and TREF results are influenced by the low molecular weight, fraction—below 10,000 g/mol,²⁰ it is not possible to determine the CCD of ethylene and α -olefins copolymers having a bimodal MWD with only CRYSTAF or TREF techniques. Therefore, bivariate distribution of molecular weight and chemical composition are necessary needed to fully describe the CCD of multimodal MWD copolymers. This is typically achieved via cross fractionation techniques, for example, by using a-TREF-GPC^{21,22} or two-dimensional high performance liquid chromatography (2D-HPLC).²³

In this article a new approach is presented which enables to differentiate, compare, and quantify the performance of different catalyst systems in regards to Chemical Composition with only one CRYSTAF experiment. By applying this new approach to the results of two-dimensional separation techniques like TREF followed by GPC [Cross Fractionation Chromatography (CFC)], CCD of complex multimodal ethylene- α -olefin copolymers can be likewise described and quantified.

EXPERIMENTAL

Solvents

1,2,5-Trichlorobenzene (TCB) used as solvent for the Crystaf and CFC was freshly distilled. 2,6-Di tert butyl-4-methyl-phenol (BHT) was obtained from Aldrich and used as it is without purification.

Samples

Over 60 unimodal and multimodal ethylene- α -olefin copolymers, which includes commercial and experimental ethylene-co-hexene and ethylene-co-butene copolymers, with comonomer content up to 5 mol % are examined in this study. In this study the polymerizations were performed by using two typical commercial ZN polyethylene catalysts, catalyst **1** is a high yield precipitated MgCl₂-TiCl₄-based catalyst with a Ti content of 7 wt %, where catalyst **2** is a SiO₂-based catalyst containing MgCl₂-TiCl₃-TiCl₄-Al(OR)₃ with a Ti content of 2 wt % as described by Garoff *et al.*²⁴

The comonomer amount for all samples was determined by ¹³C melt-state NMR. Details of the NMR method are stated elsewhere.²⁵

GPC

A high temperature chromatograph GPCIR (PolymerChar, Valencia, Spain), equipped with a four band infrared detector (IR5) was used for the determination of the molecular weight distribution. The chromatographic separation was carried out by using 3× Agilent-PLgel Olexis columns and 1× Agilent-PLgel Olexis Guard column (Agilent Technologies, Church Stretton, UK). As sample solvent and mobile phase TCB stabilized with 250 mg/L BHT was used. The chromatographic system was operated at 160°C and at a constant flow rate of 1 mL/min. About 200 μ L of sample solution was injected per analysis. The column set was calibrated using universal calibration with narrow molecular weight distributed polystyrene (PS) standards in the range of 0.5 to 11,500 kg/mol. Mark Houwink constants for PS, PE, and PP used are as given in literature.²⁶ Data collection was performed by using the PolymerChar GPC-IR control software.

Crystaf

A Crystaf apparatus model 200 (PolymerChar, Valencia, Spain) was used for the fractionation at a cooling rate of 0.1 K/min. About 15 mg of the polymer sample was dissolved in 40 mL stabilized TCB (stabilized with 250 mg/L BHT) at 160°C. An IR detector monitoring the absorption of the C-H stretching vibration was used.

Cross Fractionation Chromatography (a-TREF X SEC)

All samples were analyzed using a full automated CFC to determine the chemical heterogeneity of this sample and to be able to determine the molecular weight distribution and the corresponded molecular weight averages (M_n , M_w , and M_v) at a certain elution temperature.

A CFC instrument (PolymerChar, Valencia, Spain) was used to perform the cross-fractionation (TREF x SEC).²² A four band IR5 infrared detector (PolymerChar, Valencia, Spain) was used to monitor the concentration. Around 50 mg of the polymer sample was dissolved in 40 mL TCB in the stainless steel vessel for 180 min at 160°C. Once the sample was completely dissolved an aliquot was loaded into the TREF column and stabilized for a

Table I. Experimental Parameter of CFC Analysis

Dissolution temperature (°C)	Dissolution time (min)	Cooling rate (°C/min)	Elution steps
160	180	0.07	24 elution steps from 30°C to 140°C

while at 110°C. The following analytical parameters were chosen for analyzing the sample (Table I).

A discontinuous elution process is performed using following temperature profile. The temperature profile is shown in Figure 1.

In the second dimension (GPC) 3 PL Olexis columns 1 × Olexis Guard columns from Agilent (Church Stretton, UK) were used as stationary phase. As eluent TCB (stabilized with 250 mg/L BHT) at 150°C and a constant flow rate of 1 mL/min were applied. The column set was calibrated using universal calibration (according to ISO 16014-2:2003) with at least 15 narrow MWD PS standards in the range of 0.5 to 11,500 kg/mol. Mark Houwink constants for PS, PE, and PP used are as given in literature.²⁶

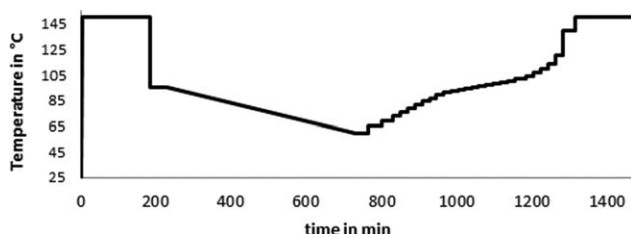
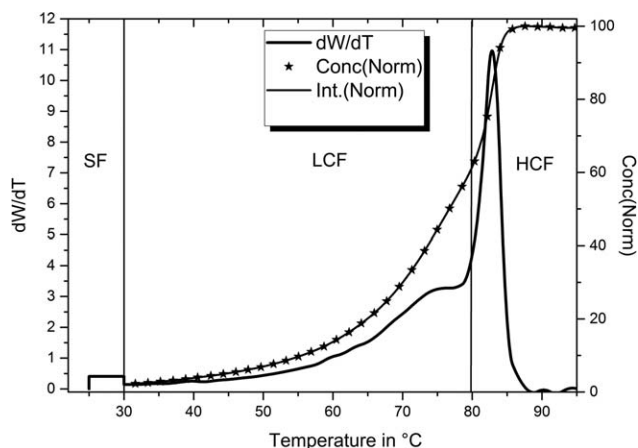
RESULTS AND DISCUSSION

Unimodal ZN-LLDPE

A very simple approach to obtain quantitative results from a Crystaf profile is the differentiation between “high crystalline fraction” (HCF), “low crystalline fraction” (LCF) and the soluble fraction at 30°C (SF). The HCF can be, for example, calculated by determining the area under the Crystaf profile from the cumulative fraction in a fixed temperature range from 80°C to 95°C or alternatively from 75°C to 95°C (Figure 2).

During this study, unimodal ethylene and α -olefin copolymers polymerized with different catalyst systems, comonomer content, and type were analyzed with CRYSTAF and the corresponding HCF, LCF, and SF were determined. In Figure 3 the HCF from ZN-LLDPE with 1-hexene or 1-butene as copolymer polymerized with different catalyst system were calculated and plotted in regards to their comonomer content.

As expected for all catalyst systems and comonomer types a decrease of the HCF with increasing comonomer amount was observed. Ethylene and α -olefin copolymers with 1-butene as comonomer always have a lower HCF compared with the 1-hexene grades having the same comonomer content. The HCF can also be affected by the ZN catalyst used for polymerization as it can be observed from Figure 2(c). The effect of the cocatalyst on the HCF in actual study can only be observed for

**Figure 1.** Temperature profile of CFC analysis.**Figure 2.** CRYSTAF profile presenting SF (soluble at 30°C in TCB), LCF (crystallize between 80°C and 30°C) and HCF (crystallizes at $T > 80^\circ\text{C}$).

the ethylene–butene copolymers where the HCF of the ethylene–hexene copolymers was not influenced significantly by the choice of the cocatalyst. These results clearly show that this simple approach enables to study the effect of various catalysts and cocatalysts on the CCD. In addition to the HCF the broadness of the low crystalline fraction is of high interest for a detailed structural characterization of ZN-LLDPE. The broadness of the LCF can be used to describe the CCD of the copolymer fraction in LLDPE and therefore enables the possibility to further study different catalyst systems performance in regards to CC in more detail (Figure 4).

The new approach was developed to describe the breadth of copolymer fraction by improving the approach from Kolb *et al.*¹⁵ As first step to describe the broadness of the LCF and SF in more detail, HCF is neglected.

The subsequent steps are carried out to determine the copolymer temperature breadth (80°). The area below the CRYSTAF profile up to 80°C is normalized to 100%, which is the area of interest to describe the broadness of the LCF. Next the temperatures at which 25% (T1) and 75% (T2) of the LCF + SF are crystallized were calculated. The copolymer temperature breadth (CTB₈₀) is then obtained by subtraction of T2 from T1.

$$\text{CTB}_{80} = T1 - T2 \quad (1)$$

In Figure 5 the CTB₈₀ of the same unimodal ZN-LLDPE with 1-butene [Figure 5(a)] and 1-hexene [Figure 5(b)] as copolymers polymerized with different catalyst systems are calculated and plotted against the comonomer content.

Figure 5 clearly shows that the CTB₈₀ value is able to differentiate between the different catalyst systems for both ethylene-1-butene and in ethylene-1-hexene copolymer samples. CTB₈₀ value is higher for catalyst system 1 compared with catalyst system 2 indicating that catalyst system 1 displays a broader CCD compared with catalyst system 2. In opposite to the work of Garoff *et al.*²⁴ which concludes from a-TREF and DSC results for ethylene-1-hexene copolymers produced with catalyst 1 and 2 the same CCD, the new approach differentiates the performance of the two catalysts in regards to the CCD. For ethylene-1-hexene copolymers, the smallest CTB₈₀ value was obtained for catalyst system 2 with cocatalyst B indicating the

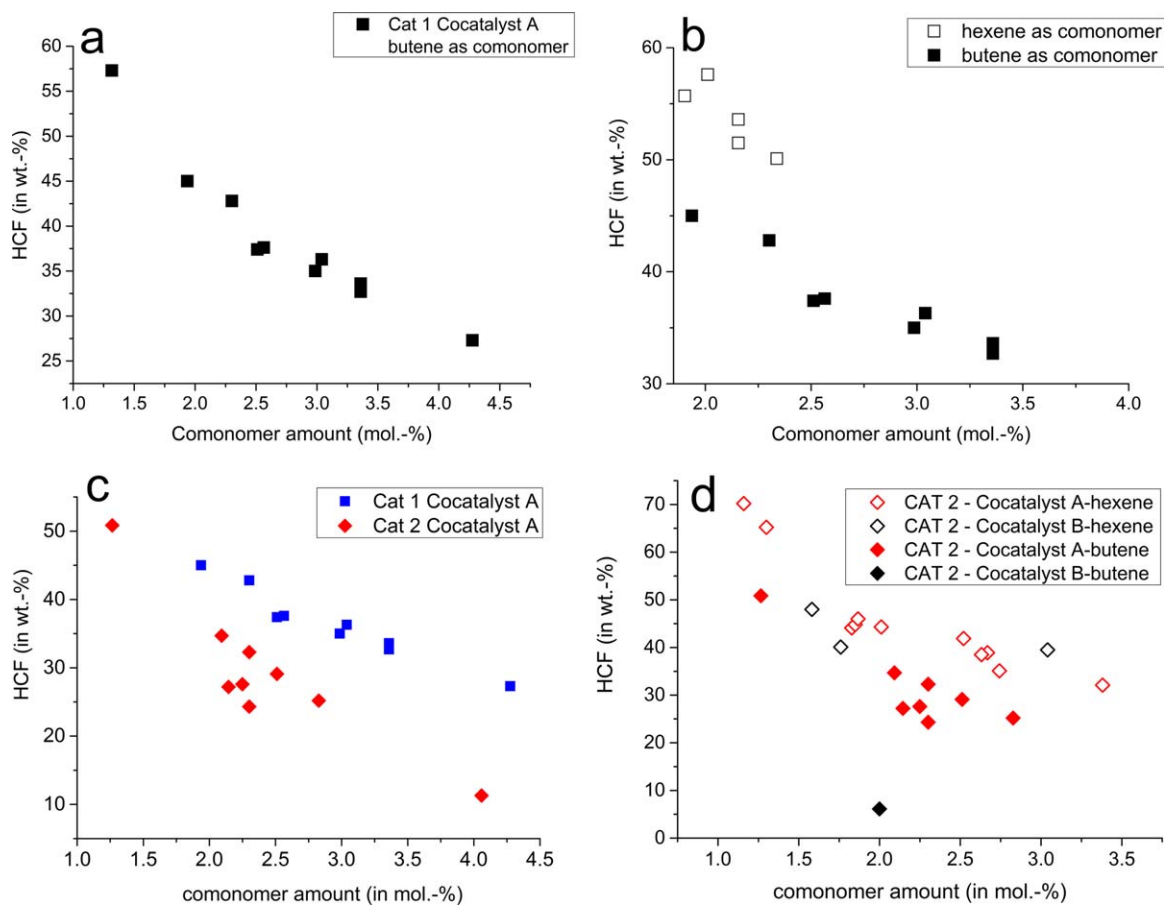


Figure 3. Dependence of HCF from CRYSTAF measurement from comonomer amount (a), comonomer type (b), catalyst type (c), and cocatalyst (d). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

narrowest CCD for a similar comonomer content and type. Similar to the HCF the CTB_{80} value also shows a higher value for ethylene-1-hexene copolymers compared with ethylene-1-butene copolymers indicating a broader chemical composition distribution for ethylene-1-hexene copolymers for the same comonomer amount. An

analogous observation was made by H.J. Assumption *et al.* where an increased heterogeneity of the polymer structure was found for the ethylene-1-hexene copolymer using preparative TREF followed by ^{13}C -NMR.²⁷ Additionally a strong effect of the catalyst system on the chemical heterogeneity is reported. An increased chemical heterogeneity is found for catalyst system 1 compared with catalyst system 2 and it is illustrated by the higher CTB_{80} value. Interestingly the cocatalyst also can increase or decrease the CCD and therefore influence the chemical heterogeneity of the polymer.

The observed higher CTB_{80} value with increasing average mol fraction of comonomer is in good agreement with the work of Sarzotti *et al.*²⁸ Also from theoretical point of view this behavior can be explained by Stockmayer's bivariate distribution.²⁹ Similar observations are observed for the CTB_{80} of all ZN catalyst systems [Figure 5(a, b)]. By applying a mathematical function that describes the relationship between CTB_{80} and comonomer amount an index can be calculated which is independent of the comonomer content and can be directly linked to the catalyst system (Table II).

For the ethylene-1-butene copolymers an exponential dependence of CTB_{80} and comonomer content (comonomer content between 1 and 5 mol %) could be found. This dependence can be used to define a copolymer temperature breadth index by using the following equation:

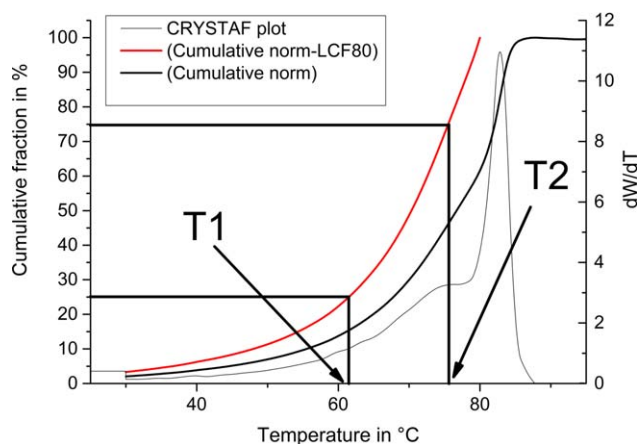


Figure 4. Graphical determination of $T_{75}-T_{25}$ value (black), CTB_{80} value (red) from the corresponded normalized cumulative curves. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

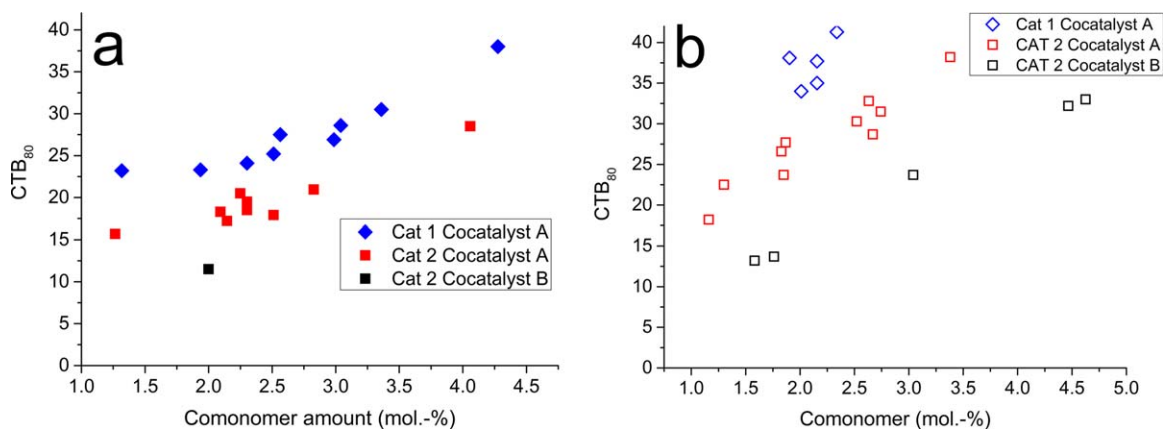


Figure 5. CTB_{80} dependence in regards to comonomer amount in mol % for ethylene-1-butene copolymers (a) and ethylene-1-hexene copolymers (b) polymerized with different catalyst systems. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$CTBI_{80} = \frac{CTB_{80}}{e^{0.2x}} \quad (2)$$

where x is the mol fraction of the comonomer in the polymer.

The following $CTBI_{80}$ values for the corresponding catalyst systems could be calculated.

Both, the $CTBI_{80}$ and the CTB_{80} values prove that by using the catalyst system 2 and cocatalyst B the narrowest CCD are obtained for the analyzed ZN-LLDPE samples. A still lower value of $CTBI_{80}$ around 5 is expected for SS-LLDPE. Therefore $CTBI_{80}$ value can be used for comparison and differentiation between various ZN catalyst systems according to the CCD. It is possible to describe the influence of the ZN catalyst on the CCD semiquantitatively with a single CRYSTAF experiment.

To determine the repeatability of the CTB_{80} , the HCF and the LCF, a bimodal ZN-LLDPE and SS-LLDPE were measured 20 times over a time period of 2 years. Results are shown in Table III.

From the calculated relative standard deviation (RSD), which is below 5% for the CTB_{80} , the HCF, and the LCF parameter, the relative differences in the CTBI between the catalyst systems, which are between 15% and 20%, are statistically significant.

Molecular Weight Influence

Nieto *et al.* determined that a shift of the peak maximum temperature in CRYSTAF analysis can be observed for molecular weights below 10,000 g/mol for homo PE.²⁰ In addition a broadening of the CRYSTAF peaks is observed with decreasing M_n value, for M_n values below 50,000 g/mol.¹⁹

The effect of the low molecular weight fraction on the $CTBI_{80}$ was studied by plotting the correlation between the amount of polymer fraction having M_w below 10,000 g/mol and the $CTBI_{80}$ value (Figure 6).

From Figure 7 no significant effect of the M_w on $CTBI_{80}$ can be observed for polymers which have between 1 and 14 wt % of molecular weight fraction below 10 kg/mol. For polymers with a high amount of low molecular weight fraction (~20 wt %) a significant effect of the low molecular weight fraction on the CTBI can be observed. This is clearly observed for a polymer sample with 20 wt % of a polymer fraction with an M_w below

10 kg/mol. For this sample a significant higher $CTBI_{80}$ value is obtained (16) as expected for the corresponded catalyst system (between 10 and 12). For polymers with a lower amount than 1 wt % of molecular weight below 10 kg/mol the $CTBI_{80}$ becomes smaller, likely due to the absence of low molecular weight fraction and the corresponding peak broadening in CRYSTAF analysis.

Multimodal ZN-LLDPE

Due to the molecular weight influence of CRYSTAF results and therefore the $CTBI_{80}$ values (see Figure 7) above described approach for CCD quantification needs to be modified in a way that low molecular weight fraction is excluded from the calculation of the $CTBI_{80}$ value. The CCD of multimodal LLDPE or HDPE potentially can be obtained by using 2-dimensional separation techniques, which determines the bivariate distribution of the polymer. Possible methods are 2-dimensional high temperature HPLC or a hyphenated a-TREF with high temperature GPC analysis; that is, CFC.

In the bivariate distribution of a multimodal ZN-LLDPE (Figure 8) the low molecular weight homo-PE fraction can be differentiated from the high molecular weight fraction and also the major part of the copolymer fraction.

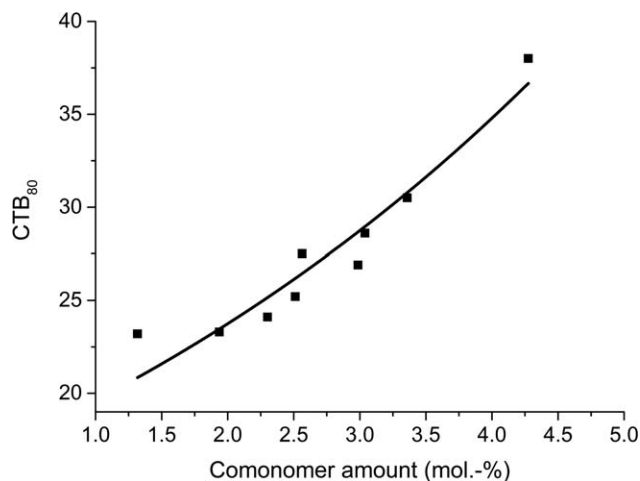
To distinguish between the copolymer fraction and the homo-PE fraction in a multimodal ZN-LLDPE, a well characterized broad homo-polyethylene (PE) sample was analyzed with the same analytical set up in a first step. The area where homo PE is not showing any signal is therefore assigned to be the area of the copolymer fraction. The CFC contour plot of homo-PE is presented in Figure 9.

Table II. $CTBI_{80}$ Values for the Analyzed Catalyst/Cocatalyst Systems

Catalyst system	$CTBI_{80}$	$CTBI_{80}$
	Ethylene-1-hexene ZN-LLDPE	Ethylene-1-butene ZN-LLDPE
Cat 1-Cocat A	22-25	14-16
Cat 2-Cocat A	16-19	10-12
Cat 2-Cocat B	10-13	6.7

Table III. Repeatability of CTB₈₀, HCF, and LCF from Crystaf Experiments

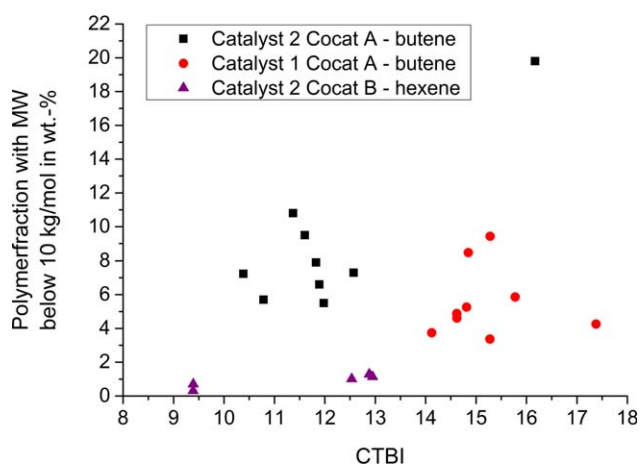
	SS-LLDPE		ZN-LLDPE	
	CTB ₈₀ average	RSD in %	CTB ₈₀ average	RSD in %
LCF (80°C)	38,7	2,2	22,8	3,5
HCF (80°C)	60,0	1,7	61,0	1,9
CTB ₈₀	13,4	4,5	35,0	4,1

**Figure 6.** Mathematical fit for ethylene-1-butene copolymers of catalyst system 1.

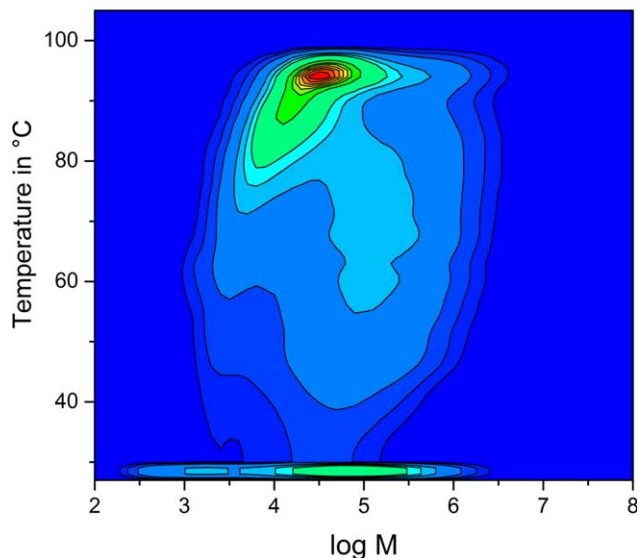
From Figures 8 and 9 separate homo and copolymer areas can be assigned. Homo PE is assigned to elute above 90°C. The following relationship needs to be fulfilled for polymer fractions eluting below 90°C in the CFC analysis:

$$\log M(T_{el}) < (T_{el} + 230)/80 \quad (3)$$

All fractions not considered to be homo polyethylene are defined to be copolymer. The copolymer fraction of the ZN-LLDPE determined by this approach is shown in Figure 10.

**Figure 7.** Molecular weight dependence of CTBI₈₀ value. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ZN-LLDPE

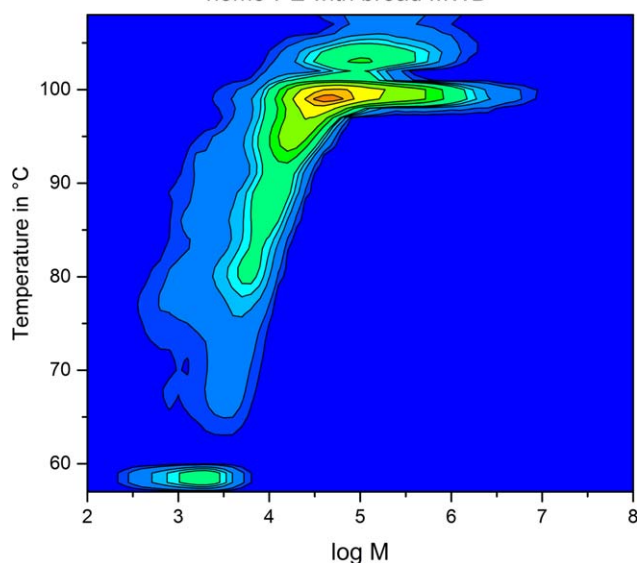
**Figure 8.** CFC contour plot of ZN-LLDPE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In the second step, the broadness of the CCD of the copolymer fraction is described quantitatively. Here a similar approach is applied as used previously for the unimodal ZN-LLDPE samples where the temperature difference between the temperature at which 25% and the temperature at which 75% of the copolymer fraction is eluted is calculated. Therefore, the amount of the copolymer fraction needs to be normalized to 100 (Figure 11).

The copolymer temperature breadth (CTB_{copo}) can be then calculated as:

$$CTB_{copo} = T1 - T2 \quad (4)$$

homo-PE with broad MWD

**Figure 9.** CFC contour plot of homo PE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

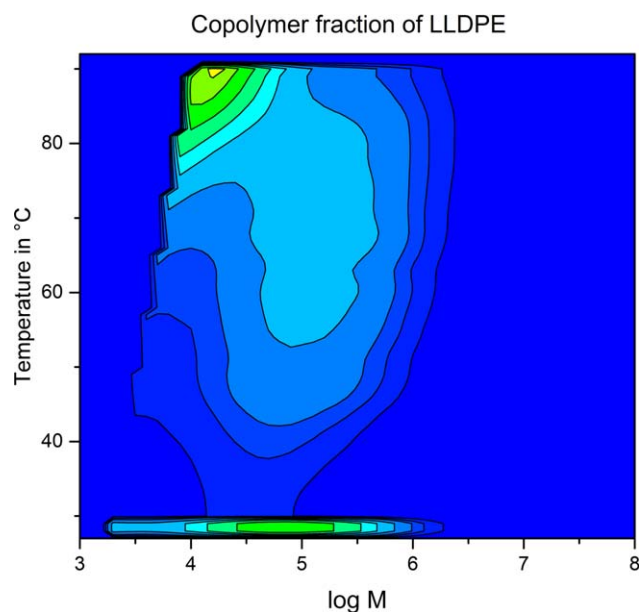


Figure 10. CFC-contour plot of the copolymer fraction. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The CFC contour plots of two ethylene-butene copolymers with similar butene content (0.56/0.45 mol %, respectively, for cat1 and cat2) are shown in Figure 12.

Both samples show the typical heterogeneity expected for a multimodal HDPE grade produced with ZN catalysts. Both samples have a strong molecular weight dependence on the elution behavior in the TREF separation (1st dimension) for $\log M$ below 4.2 as expected. For $\log M$ higher than 4.5 the typical CCD of ZN-C2/C4 copolymer samples with a homo-PE peak between 90°C and 102°C and a comonomer fraction between 60°C and 90°C and a fraction which does not elute at 60°C (SF) was observed. For the sample produced with catalyst 1

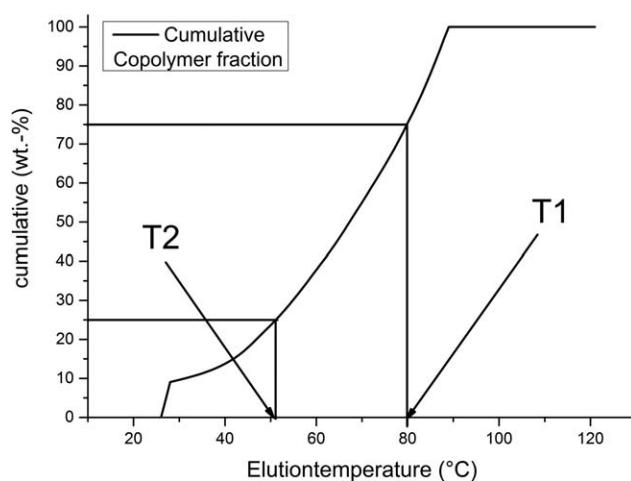


Figure 11. Cumulative copolymer fractions along the elution temperature in CFC.

[Figure 12(A)] a higher amount of the fractions which stays in solution at 60°C is observed and also a broader area of the copolymer fraction is observed compared with the sample produced with catalyst 2 [Figure 12(B)]. From the CFC contour plots the following CTB_{copo} were calculated as described above.

Similar to the unimodal-ZN LLDPE a higher CTB_{copo} value is obtained for samples polymerized with catalyst 1. This result is in a good agreement with the CTBI value observed with unimodal ZN-LLDPE. An increase of the broadness of the CCD can be observed for bimodal samples polymerized in presence of catalyst 2 for ethylene-hexene copolymers compared with ethylene-butene copolymers. The CTB_{copo} is also increasing with comonomer amount in a significant way, which is expected already from the results from the unimodal ZN-LLDPE samples [see Figure 3(a)]. Results show that the CTB_{copo} index can be used to describe and quantify the broadness of CCD of polymers with multimodal MWD and similar comonomer content (for e.g., polymers from two unknown catalysts) (Figure 13).

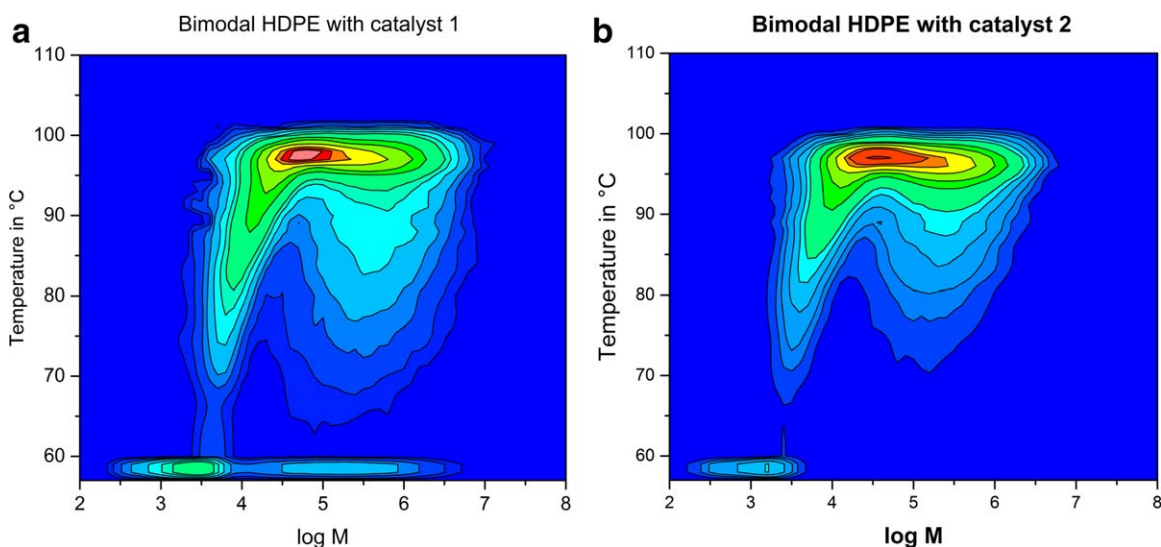


Figure 12. CFC contour plot of Bimodal HDPE samples with catalyst 1 (a) and catalyst 2 (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

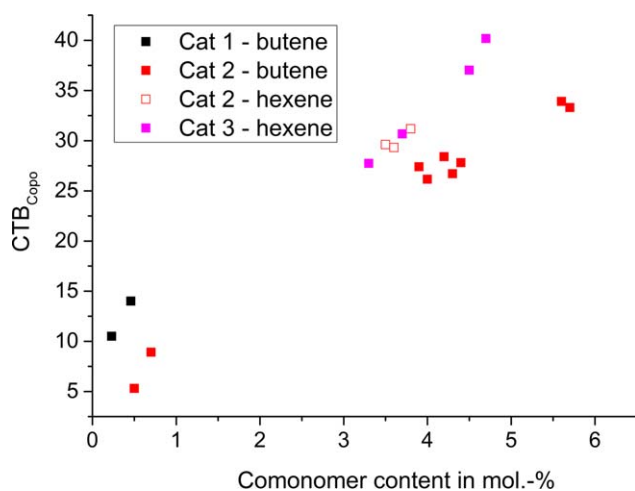


Figure 13. CTB_{Copo} of bimodal ZN PE with low comonomer content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

In this study the performance of a catalyst in regards to the CCD was studied by using Crystaf analysis of ethylene-1-hexene and ethylene-1-butene copolymers. By this new approach for quantifying the CCD of unimodal ZN-PE copolymers the differences in the CCD can be linked to the corresponding ZN catalyst systems with a single CRYSTAF experiment, if comonomer type and amount is known. For all studied catalyst systems broader CCD for ethylene-1-hexene compared with ethylene-1-butene copolymers was observed.

Applying this approach to 2-dimensional fractionation techniques like CFC the CCD of the copolymer fraction can be more accurately quantified and the effect of different ZN catalysts in multimodal polyethylene copolymers studied. In addition it is possible to distinguish between the low molecular weight homo PE fraction and the copolymer fraction in multimodal polyethylene copolymers.

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