

Comprehensive Analysis of Polyethylene Graft Copolymers by Preparative Fractionation, Interaction Chromatography, and Thermal Analysis

Paul S. Eselem Bungu, Kristina Zentel, Sascha Hintenlang, Markus Busch, and Harald Pasch*

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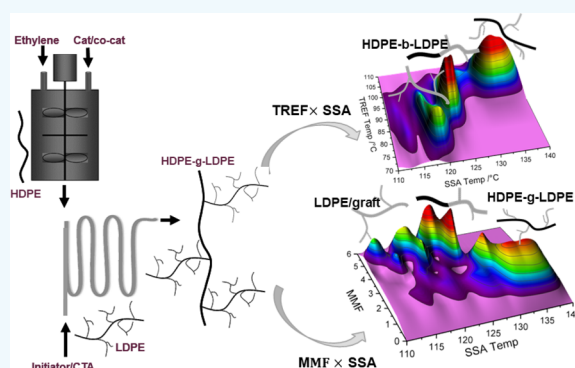
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ABSTRACT: The comprehensive analysis of complex copolymers is a challenge and requires the combination of results from different methods including size exclusion chromatography for molar mass and molecular spectroscopy for chemical composition analysis. In true copolymers, comonomers with different chemical structures are combined, resulting in various molecular compositions and topologies which can readily be identified. Different analytical challenges arise when only one monomer is used to produce complex molecular topologies. In this work, polyethylene architectures are designed by using the grafting of low density polyethylene (LDPE) onto a reactive backbone of high density linear polyethylene (HDPE). These graft copolymers consist of only ethylene repeat units. The graft copolymers are prepared by using a dual reactor setup where in the first reactor HDPE is catalytically produced. HDPE is then used as the feed for the free radical polymerization in the tube reactor. At different tube temperatures, polymers with different compositions are produced. To comprehensively analyze the molecular structure of the reaction products, they are subjected to preparative molar mass fractionation and preparative temperature rising elution fractionation. The analysis of the fractions by gradient (solvent and temperature) interaction chromatography, successive self-nucleation and annealing, and triple detection size exclusion chromatography reveals the presence of the true graft copolymer HDPE-g-LDPE along with HDPE and LDPE fractions and some HDPE-*b*-LDPE copolymer chains.

KEYWORDS: polyolefins, graft polyethylene, solvent/temperature gradient interactive chromatography, successive self-nucleation and annealing, preparative fractionation, graft microstructure



INTRODUCTION

Polyolefins with their diverse application properties have dominated the global plastics market for several decades, among them polyethylene (PE) and polypropylene (PP). The microstructure of PE comprises just ethylene repeat units ($-\text{[CH}_2-\text{CH}_2\text{]}_n-$). Although the molecular formula of PE appears to be very simple, the detailed chain structure may be quite complex with distributions in molar mass (MM), chemical composition (CC), and molecular topology. PE typically appears in three different versions, namely high density (HDPE), low density (LDPE), and linear low density PE (LLDPE). HDPE is produced catalytically and consists of mainly linear macromolecules. LLDPE is also formed in a catalytic process but exhibits short chain branching (SCB) due to copolymerization of ethylene with higher α -olefins, such as butene, hexene, and octene. In contrast, LDPE is produced by high-pressure free-radical polymerization and exhibits long chain branching (LCB) in addition to SCB. In addition to displaying broad molar mass distributions (MMD), these resins are also known to exhibit broad chemical composition distributions (CCD) with regard to short chain branching

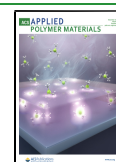
(SCBD) and long chain branching (LCBD) distributions, making them polymers with complex molecular topologies. Polyolefin plastomers/elastomers are known to contain higher comonomer contents (>10 mol %), which makes them highly amorphous, providing excellent stretching ability.¹

In addition to “true” copolymers, where chemically different comonomers are combined, complex polyolefin architectures can be prepared based on just one monomer. Such “copolymers” may be obtained by combining structures with different molecular topologies; for example, linear homopolymers could be coupled with branched homo/copolymers. One synthetic approach is the grafting of a monomer onto a reactive polymer backbone of the same monomer type.

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In the field of polyolefins, an interesting version of such “copolymer” based on just ethylene would be the combination of linear HDPE (as the polymer backbone) with branched LDPE (as the polymer grafts).^{2–4} Such materials with complex molecular topologies might possess superior application properties by combining the stiffness of HDPE with the good processability of LDPE. However, not only the synthesis but also the comprehensive molecular characterization of such “copolymer” is a significant challenge.

When designing new microstructures, it is imperative to correlate the polymeric structures to the polymerization conditions by employing advanced analytical methods. Nuclear magnetic resonance (¹³C NMR) and Fourier transform infrared spectroscopy (FTIR) provide average chemical composition and branching information for polyolefins. Chemical composition distributions of polyolefins are typically characterized by using crystallization fractionation analysis (CRYSTAF),⁵ crystallization elution fractionation (CEF),⁶ differential scanning calorimetry (DSC),^{7,8} and others. Thermal fractionation methods such as successive self-nucleation and annealing (SSA) have been developed by using DSC to segregate polyolefin macromolecules according to (linear) methylene sequence length (MSL) and tacticity.^{9,10} These techniques being crystallization based are selective toward the analysis of the crystallizable components of semicrystalline polyolefins, which of course strongly depends on branching type and distribution.

The advancement of solvent gradient interactive chromatography (SGIC) using porous graphitic carbon (PGC) stationary phases has paved new ways of probing into the microstructure of polyolefins irrespective of crystallizability.¹¹ In recent times, different solvent systems^{12,13} and varying column temperatures and column lengths¹⁴ have been applied to enhance separation of complex polyolefins. Added to that, Cong et al. developed temperature gradient interaction chromatography (TGIC) at high temperatures for the fractionation of complex polyolefins.¹⁵ While the mixed mobile phase restricts SGIC to be used with an evaporating light scattering detector (ELSD), the isocratic mobile phase renders TGIC more adaptable to other detectors.^{11,15–18}

Typically, size exclusion chromatography (SEC) is used to address the molar mass heterogeneity of complex polyolefins. Triple detection SEC (SEC-3D) which combines a concentration detector (infrared, IR, or refractive index, RI) in series with multiangle light scattering (MALS) and an online viscometer (Vis) detector enables the comprehensive analysis of branched polyolefins. In a previous study, the multiple preparative fractionation concept was introduced.¹⁹ The experimental setup incorporates the use of preparative molar mass fractionation (pMMF) and temperature rising elution fractionation (pTREF) to generate library fractions in milligram amounts that vary in molar mass (pMMF) and chemical composition (pTREF). Cross-analysis of the fractions with advanced analytical techniques provides comprehensive molecular information.

The current study focuses on the comprehensive analysis of copolymers that are produced by grafting LDPE onto a HDPE backbone (HDPE-g-LDPE).^{2–4} As clearly demonstrated in Figure 1, the investigated resins are produced in a high-pressure setup using dual reactors consisting of a continuously stirred tank autoclave (CSTR) and a tubular reactor (referred here as tube reactor) connected in series.

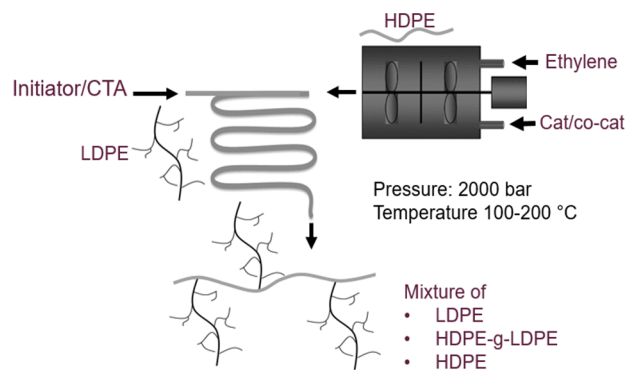


Figure 1. Scheme illustrating the dual reactor setup designed for the high-pressure polymerization of HDPE-graft-LDPE copolymers.

At pressures of 2000 bar and temperatures above 100 °C, gaseous ethylene is compressed to supercritical fluid, which acts as both the reactant and the solvent. In the first step of the process, HDPE is produced catalytically from the supercritical ethylene within the CSTR reactor by using a bis-biphenyl-phenoxy post-metallocene catalyst, and the mechanism of the catalytic process was previously discussed.^{20,21} Subsequently, free-radical polymerization of ethylene is started in the tube reactor by the addition of a thermal initiator. This leads to not only the production of branched LDPE via the high-pressure free-radical process but also the formation of graft copolymer. In this case, the content in the CSTR acts as the feed source for the proceeding reaction in the tube. The transfer of a radical functionality from a growing LDPE molecule to an HDPE molecule from the CSTR can restart polymerization to HDPE-g-LDPE copolymers as shown in the reaction scheme presented in Figure 2. It is expected that the resulting resins exhibit complex microstructures inheriting the individual properties of HDPE and LDPE in combination with the intrinsic properties of the newly formed graft copolymers.

To acquire detailed knowledge of the compositional complexity, a preliminary microstructural investigation was conducted by combining pTREF with CRYSTAF, ¹³C NMR, triple detector SEC, and two-dimensional liquid chromatography (2D-LC).²² Although the analyses revealed a complex mixture of branched and linear macromolecules, the separation and identification of the true graft copolymer fraction from the pristine LDPE remained a challenge, probably due to the fact that both species exhibit very similar microstructural characteristics in solution.

In the current work, we aim at combining gradient HPLC and SSA to identify the different types of macromolecules that are obtained by the multiple preparative fractionation protocol.¹⁹ Cross-analysis of the library fractions by gradient HPLC and SSA could help to segregate the different macromolecules according to linear ethylene sequence (LES) lengths and crystallizable methylene sequence lengths (MSL), respectively. Considering that LDPE shows a melting behavior that is distinctively different from HDPE and LLDPE, the differences regarding heat of fusion and crystallinity may provide a better pathway of distinguishing the graft copolymer chains from the HDPE and LDPE precursors. Correlating the analytical results to those of triple detection SEC may provide in-depth microstructural information to help to distinguish and identify the different polymer species. Added to that, this approach may provide detailed information about the reaction pathway of the grafting process.

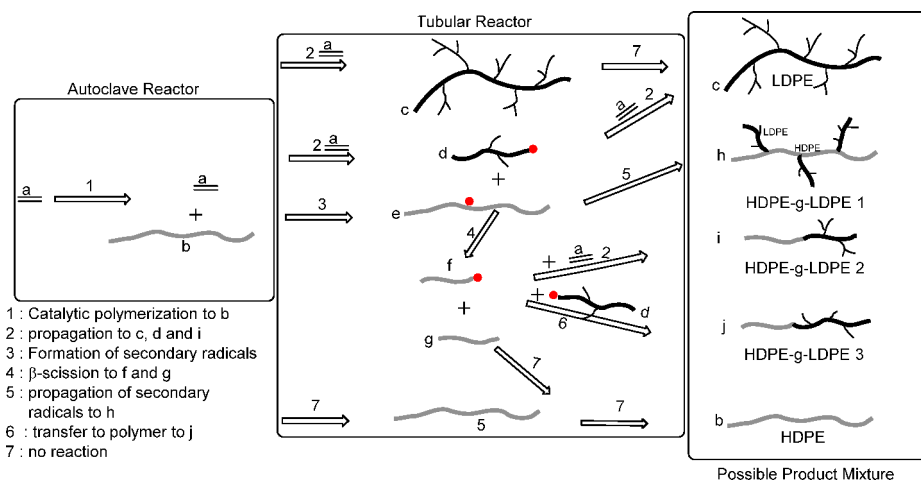


Figure 2. Reaction scheme describing possible reaction pathways and the anticipated products formed.

Table 1. Physical Properties of the Samples as Measured by Triple Detector SEC and DSC

| sample name | M_w^a (kg/mol) | D^a | M_w^b (kg/mol) | D^b | T_c^c ($^{\circ}\text{C}$) | T_m^c ($^{\circ}\text{C}$) | X^d (%) |
|-------------|------------------|-------|------------------|-------|--------------------------------|--------------------------------|-----------|
| gc115 | 66.7 | 10.9 | 80.6 | 12.7 | 115.2 | 128.6 | 77.2 |
| gc100 | 141.3 | 16.0 | 367.5 | 40.6 | 108 | 122 | 66.9 |
| LDPE | 72.5 | 15.8 | 136.8 | 27.5 | 110.6 | 120.4 | 51.0 |
| HDPE | 103.4 | 12.9 | 102.9 | 14.9 | 119.0 | 133.1 | 78.8 |
| PE S2K | 57.1 | 3.8 | 56.2 | 3.9 | 112.9 | 134.6 | 85.9 |

^aDetermined by SEC-IR5, PE equivalents. ^bAs determined by SEC-vis. ^cAs determined by DSC. ^d $\Delta H_m^c/\Delta H_m^o$, $\Delta H_m^o = 294$ J/g.

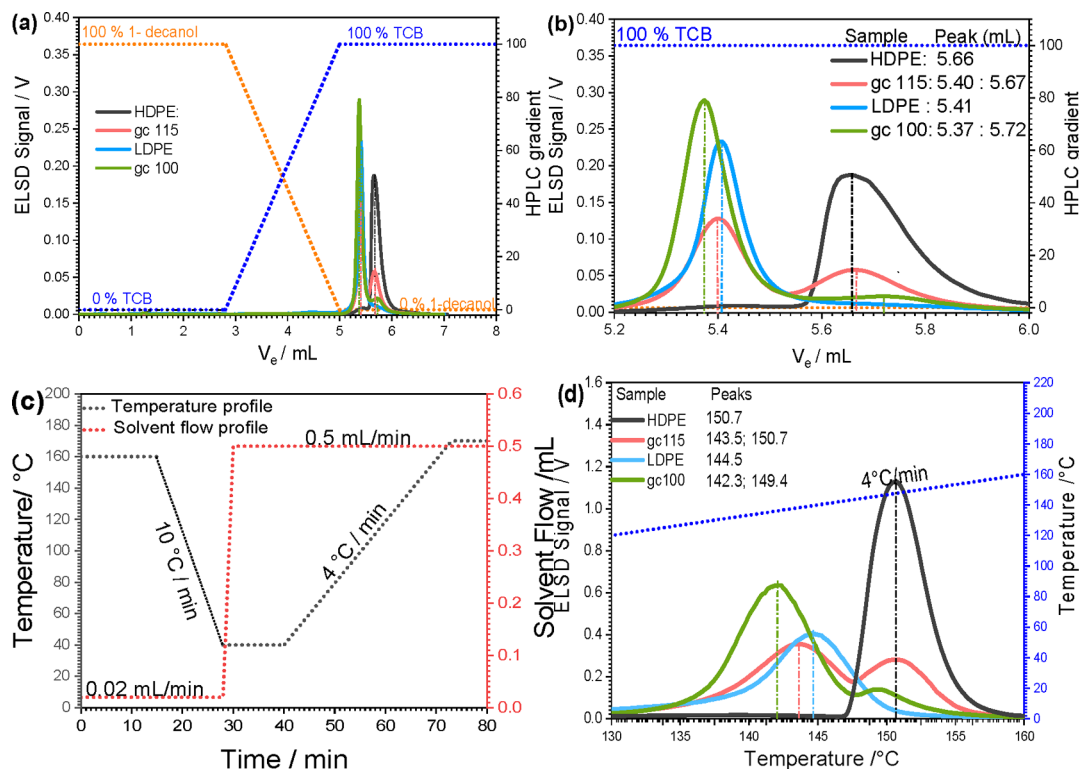


Figure 3. Plots describing in (a) SGIC and (c) TGIC experimental procedures and resulting chromatograms, SGIC in (b) and TGIC in (d), comparing the graft copolymer samples to the those of LDPE and HDPE.

EXPERIMENT AND MATERIALS

The graft polymers gc115 and gc100 and the linear (HDPE) and branched (LDPE) polyethylene analogues used in this study are laboratory products and were produced by using a combination of a continuously stirred tank reactor (CSTR) in-line with a tube reactor

under supercritical conditions (Technical University Darmstadt, Germany).^{2,3} The linear PE reference (PE S2K) was purchased from the American Polymer Standards Corporation. Except stated otherwise, 1-decanol and 1,2,4-trichlorobenzene (TCB), 1,2-dichlorobenzene (ODCB), xylene, and diethylene glycol methyl ether

(DEGME) (all Sigma-Aldrich, South Africa) were used in all analyses as received. The thermophysical properties of all samples are summarized in Table 1. For a better comparison, the experimental conditions for the preparation of gc115 and gc100 in the CSTR were the same, the only difference being that the grafting reactions in the tube were conducted at 115 and 100 °C, respectively.

The analogous linear and branched PEs were produced under similar experimental conditions. The experimental conditions for the polymerizations are given in Table S1 (see Results and Discussion). Except where stated otherwise, all experimental procedures for the different analytical instruments are provided in the Supporting Information.

Gradient Interaction Chromatography (HPLC). The gradient interaction chromatography separations were achieved according to the published method of Ndiripo et al.¹³ with slight modifications. Chromatograms were obtained in solvent gradient interaction (SGIC) and temperature gradient interaction (TGIC) modes by using the SGIC system constructed by Polymer Char (Valencia, Spain). The instrument was composed of an autosampler (which is a separate unit connected to the injector via a heated transfer line), two separate ovens, switching valves, and two pumps which were equipped with vacuum degassers (Agilent, Waldbronn, Germany). A high-pressure binary gradient pump was used.

Solvent Gradient Mode. For SGIC experiments, an evaporative light scattering detector (ELSD, model PL-ELS 1000, Polymer Laboratories, Church Stretton, England) was used with the following parameters: a gas flow rate of 1.5 SLM, 160 °C nebulizer temperature, and an evaporation temperature of 270 °C. All samples were fractionated as described in Figure 3a by using a 100 × 4.6 mm i.d. Hypercarb column (Hypercarb, Thermo Scientific, Dreieich, Germany) packed with porous graphite particles (particle diameter: 5 μm; pore size: 250 Å; and surface area: 120 m²/g). The column temperature was maintained at 160 °C in the column oven. The mobile phase flow rate was 0.5 mL/min. To achieve separation, a linear gradient was applied from 100% 1-decanol to 100% TCB within 10 min after sample injection. The conditions were held for 20 min before re-establishing 1-decanol to 100%. Samples were injected at a concentration of 1–1.2 mg/mL by using a 50 μL injection loop.

Temperature Gradient Mode. Separation in TGIC was achieved by using ODCB as the mobile phase. The same ELSD detector for SGIC was used with an evaporation temperature of 230 °C. The temperature and the mobile phase flow profiles with detailed modification of the mobile flow rate and the temperature gradient are described in Figure 3c. For convenience, the elution volumes are corrected to start at 0 mL from the point when the solvent flow rate was increased from 0.02 to 0.5 mL/min. This means that the injection of the samples and column cooling for all experiments was done in 0.6 mL, which corresponds to a time of 30 min at a flow of 0.02 mL/min. Based on this, the elution volume for all experiments was converted to elution temperature via eq 1, where r_t , e_{t1} , e_{t2} , T , and e_T are the heating rate, elution time at which the flow rate was increased, the elution time at the start of the column heating, the column temperature at the start of the gradient, and the elution temperature.

$$(2r_t) \times (e_{t1} - e_{t2}) + T = e_T \quad (1)$$

All other (standard) experimental procedures, including triple detection SEC, all DSC experiments, pMMF, and pTREF, are presented in the Supporting Information.

The ethylene polymerization and grafting details are also given in the Supporting Information.

RESULTS AND DISCUSSION

Proposed Reaction Pathways. As shown in the reactor scheme in Figure 1, the investigated resins were produced by using dual reactors consisting of a CSTR and a tube connected in series. According to the reaction scheme in Figure 2, the ethylene (a) catalyzed reaction occurring in the CSTR produces HDPE (b). A detailed experimental procedure on

the polymerization process was previously reported²² and is provided in the Supporting Information, while the experimental conditions and the reagent concentrations used are summarized in Table S1.

Thereafter, HDPE (b) and some unreacted ethylene move to the preheated, prepressurized tube reactor that is subjected to a constant initiator/CTA flow. The reaction proceeds first with an initiator radical attacking ethylene to form monomer radicals and subsequent propagation giving macroradicals (d), which might terminate to form dead LDPE molecules (c) similar to a classical high pressure free-radical process.^{23,24} Additionally, the macroradicals can attack the HDPE molecules present in the reaction mixture and produce secondary radicals (e), which can further undergo β -scission to form two smaller macromolecules: a primary radical (f) and a dead HDPE molecule (g). If (f) continues propagation or termination with the LDPE macroradicals (d), HDPE-*b*-LDPE block copolymers (i) or (j) might result. Alternatively, the secondary radical (e) may undergo subsequent propagation to graft copolymer with a HDPE backbone and LDPE side branches (h). Any unreacted HDPE from the CSTR may result in linear PE chains in the final product mixture. Ideally, the final product will constitute a mixture of the (pristine) “homopolymers” HDPE and LDPE, block copolymers (HDPE-*b*-LDPE), and the graft copolymer chains HDPE-*g*-LDPE with characteristic broad molar mass and topological distributions.

Typically, batch analysis of complex polymers provides average microstructural information. On the other hand, SEC provides information regarding molar mass heterogeneity, while CRYSTAF and DSC provide information regarding the chemical composition heterogeneity in solution and melt, respectively. A preliminary investigation that combined triple detection SEC, CRYSTAF, NMR, and 2D-LC undoubtedly revealed a complex mixture of branched and linear macromolecules.²²

The current study is tailored toward the separation and identification of the different polymer species of the constituting product mixture by combining gradient HPLC with SSA and triple detection SEC (SEC-3D). As earlier mentioned, HPLC and SSA separate macromolecular chains based on differences in linear ethylene sequences (LES) and crystallizable methylene sequence lengths (MSL), respectively. These molecular characteristics have shown to have a direct correlation with the branching structure.^{9,25}

HPLC Analysis of Bulk Resins. In the first set of experiments, the graft copolymer samples gc100 and gc115 and the (pristine) homopolymers HDPE and LDPE are investigated by SGIC (SGIC_{10min}) on PGC using a 1-decanol to TCB solvent gradient. The experimental procedure (solvent gradient) and the resulting elugrams are presented in Figure 3a, and the enlarged elugrams of the samples are shown in Figure 3b. Details on the separation mechanism of polyolefins on PGC have been presented before.²⁶ For comparison, the chromatograms of HDPE and LDPE are plotted alongside the graft copolymer samples. In agreement with the expected behavior of LDPE and HDPE, the mostly linear HDPE exhibits the strongest interaction with the stationary phase and elutes last at an elution volume of 5.66 mL. Because of its branching structure, LDPE shows weaker interactions with the stationary phase and elutes at a lower elution volume of 5.40 mL. While the LDPE displays a unimodal elugram, HDPE exhibits a characteristic bimodality with the main peak typical

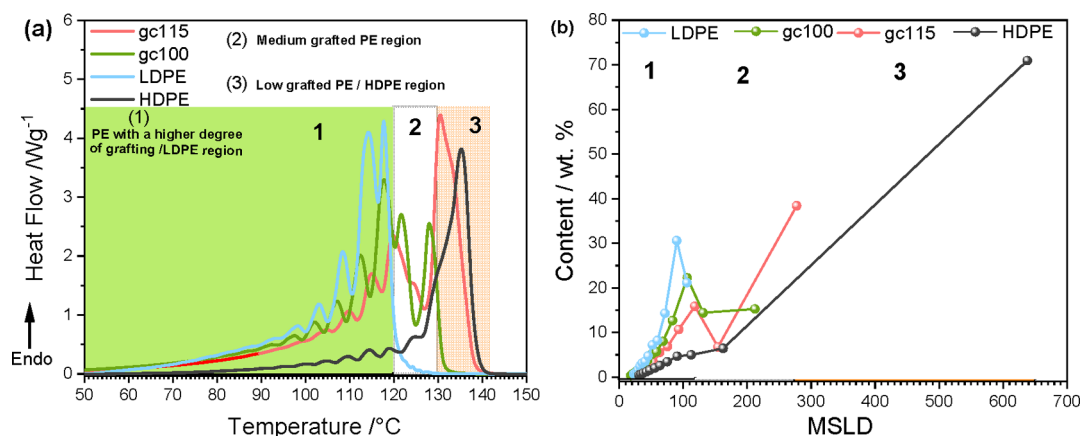


Figure 4. Superimposed SSA melting endotherms (a) and methylene sequence distribution plots (b) comparing crystal size distributions differences between the graft copolymers (gc115 and gc100) and the pristine homopolymers (HDPE and LDPE). Three temperature regions (1–3) are defined and discussed in the text.

of linear chains and a small peak with an elution volume typical of the branch polymer (see Figure 3b). The low retention peak might be due to the molar mass effect or branching. The behavior is expected since the bis-biphenyl-phenoxy post-metallocene catalyst used in the synthesis was reported to produce tiny amounts of branched PE due to thermal initiation.^{20,21}

The comparison of the elution behaviors of HDPE and LDPE to those of the graft copolymers provides some first interesting structural information. Both gc115 and gc100 display bimodal elugrams with peak elution volumes around 5.4 and 5.7 mL, indicating the presence of branched and rather linear fractions, respectively. Both graft copolymer samples were produced under similar experimental conditions, the only difference being the higher reactor temperature of the tube for sample gc115. In the case of gc100, a bimodal elugram is seen with a principal peak at 5.37 mL, which is a clear indication of branched macromolecules with a high level of branching.

According to the SGIC separation principles, the smaller peak seen around 5.72 mL can be attributed to PE chains with long linear ethylene sequences similar to the structures seen in HDPE. On the basis of these findings, it can be concluded that sample gc100 constitutes a mixture of branched and linear species having distinct molecular topologies. In comparison, sample gc115 also showing a bimodal elution profile seems to contain a higher amount of rather linear molecules and a smaller amount of branched molecules. Besides, the shift of the first eluting peak of gc100 toward lower elution volumes is indicative of a slightly higher level of branching/grafting as compared to gc115 and LDPE. The observed differences in the elution behaviors of the samples that are based on their elution profiles do not tell much about their topological differences, hence the challenge to distinguish LDPE and graft copolymer molecules HDPE-g-LDPE. It is equally challenging to distinguish the exact molecular structure of the presumed linear species of the graft copolymer samples from that of HDPE. In addition, the relatively narrow separation window in SGIC (3 mL from the start of the gradient) enhances coelution of polymer chains having small differences in the level of branching/grafting.

Aiming at enhancing the separation of the different molecular structures, the samples were further investigated by using TGIC. This technique exhibits a wider separation window that ranges from the dissolution temperature of the

samples to about 170 °C. Typically, the dissolution temperature of linear PE molecules ranges from 95 to 100 °C, while their branched counterparts dissolve between 75 and 80 °C in TCB and ODCB.^{9,27}

In the presence of the stationary phase (PGC), elution volumes are seen that correspond to higher temperatures due to strong van der Waals interactions with the PGC particles of the stationary phase. Several studies reported a range of elution temperatures (130–160 °C) for HDPE, which is dependent on the experimental conditions applied as well as the desorbing strength of the mobile phase.^{15–18}

The experimental procedure applied for the TGIC analysis of the current samples is presented in Figure 3c, and the elugrams of the samples are shown in Figure 3d. As is seen, HDPE and LDPE display peak elution temperatures at about 150.7 and 144.5 °C, respectively. In the case of gc115, two eluting peaks of almost equal peak intensities are seen at 143.5 and 150.7 °C, indicating a mixture of branched and linear species, respectively. In contrast, gc100 displays a bimodal elugram with peak temperatures at 142.3 and 149.4 °C, showing peak temperature shifts of 2.1 and 1.3 °C toward lower temperatures for the branched and linear species, respectively, indicating a higher level of branching. When comparing the elution profiles in SGIC and TGIC, better separation of molecules of the graft copolymer from LDPE is evident in TGIC. Despite observing improvements in the separation of the analyte species in TGIC, both techniques still suffer from coelution effects.

SSA Analysis of Bulk Resin. To provide more insight into the microstructural complexity of the samples, their molecular structures were further investigated through SSA, which is a thermal fractionation technique that segregates molecular species with similar crystallizable methylene sequences into nuclei or seeds. Details on the experimental procedure are provided in the Supporting Information. These seeds are formed by repeated annealing of the polymer samples by successively decreasing the self-nucleation temperatures (T_s) beginning with the ideal T_s . Prior to the SSA analysis, a self-nucleation experiment is conducted on each sample as described in the work of Müller and others to enable the determination of the ideal T_s .^{28,29} In the current work, the self-nucleation experimental protocol described in ref 9 was used for the determination of $T_{s,ideal}$ of each sample (see Table S3). $T_{s,ideal}$ is the lowest temperature at which polymer chains self-

nucleate without annealing, allowing the polymer chains to form nuclei at various T_s heating cycles.⁹ At the final SSA heating cycle, melting endotherms with multiple peaks are obtained for heterogeneous polymers as shown in Figure 4a. Here, each peak represents a nucleus or a seed consisting of a group of polymer chains with similar crystallizabilities or thermodynamic stabilities. As expected, the graft copolymer samples show greater heterogeneity at the lower temperatures region in comparison to HDPE.

Added to that, the seed distribution of the samples is significantly different. To interpret the plots in Figure 4a conveniently, the plot area is divided into three temperature regions labeled 1–3. Depending on the type of catalyst used during the synthesis, HDPE typically exhibits melting events between 130 and 140 °C due to the availability of chains with longer linear methylene sequences (see the shaded area labeled 3).^{9,30,31} The low-temperature domain is characterized by the incorporation of a tiny amount of side chains, while the upper temperature limit constitutes mainly the perfect linear chains. Melting events in the temperature region labeled 1 are characterized by polymer chains with a high degree of branching such as in LDPE.^{9,30,31} The area labeled 2 covers the temperature region typical of PE copolymers as was previously discussed by Zhang et al.³² Inspecting the SSA plot of HDPE, it is seen that the main peak melting temperature is ~135 °C, which is characterized by the linear PE backbone.^{9,33} The series of melting peaks observed between 125 and 100 °C may be attributed to PE chains with a certain degree of branching and/or a low molar mass (compare branching and mass of MMF fractions of HDPE are shown in Table S2). The main peak of gc115 is seen at 130.2 °C. Even though the peak temperature is slightly lower than that of HDPE, it characterizes linear PE chains with a very low level of branching. This sample also exhibits a significant number of peaks with low intensities within region 1, suggesting the presence of macromolecules with LDPE backbone or copolymer chains with a higher level of branching. In the case of sample gc100, no peak is seen within region 3, indicating the absence of HDPE macromolecules. The peaks at 121 and 128 °C are attributed to the graft copolymer chains with different levels of grafting, whereas the peaks in region 1 are either associated with (pristine) LDPE or graft copolymer chains with a higher level of grafting or a mixture of both. Here, for the first time, macromolecules with melting characteristics different from the (pristine) LDPE and HDPE structures are identified, suggesting the presence of graft copolymer chains HDPE-g-LDPE in the samples. To quantitatively measure the different polymer species, the peak area of each peak was converted to seed content (in wt %) by using the method proposed by Müller et al.¹⁰ and others.^{9,31} The peak melting temperatures of the various seeds were converted to methylene sequence lengths (MSLs) by using the calibration approach proposed by Keating.³⁴ By applying the equations of Zhang,³² we determined the MSL for all samples. Plots of MSL vs percentage seed content comparing the MSL distribution (MSLD) of the different samples are presented in Figure 4b. In agreement with previous SSA experiments, maximum average MSLs of 604 and 81 carbon atoms (C_{604} and C_{81}) were reported for the HDPE standard (PE 52K) and a commercial LDPE sample, respectively.^{9,31,30} In the case of the present HDPE sample, an average MSL of C_{666} is recorded for the principal peak, in comparison to the C_{277} and C_{212} observed for gc115 and gc100, respectively. Accordingly, these results,

indicate that the main peak of the HDPE SSA profile is mainly due to linear PE chains, while those of gc115 and gc100 may be associated with graft copolymer molecules with different degrees of grafting. By converting the highlighted temperature areas in Figure 4a to MSL as indicated in Figure 4b, it seems that the average MSL of each seed increases with an increase in the peak temperature. Even though the principal peaks of HDPE and gc115 are seen in the same temperature region (3), their MSLs, as well as their peak distributions, are significantly different, suggesting differences in their crystal sizes and crystal size distributions. Here, a lower MSL is synonymous to a higher level of branching/grafting as was previously discussed.⁹ Although the melting peak area assigned as 1 shows a broader temperature range as compared to 2 and 3 (Figure 4a), which is indicative of intermolecular heterogeneity, a rather narrow methylene sequence length distribution (MSLD) is seen, indicating intramolecular homogeneity. On the contrary, molecules melting in regions 2 and 3 exhibit increasing heterogeneities in MSL despite showing narrow distributions in melting temperatures. Here, it can be concluded that molecules of gc100 exhibit a higher level of branching/grafting as compared to gc115. This statement is in agreement with the reported HPLC results (see Figure 3). Even though combining gradient HPLC and SSA appears to be helpful in the identification and quantification of the different polymer species, these techniques show limitations when attempting to correlate the observed HPLC and SSA results to molar mass, viscosity, radius of gyration, and long chain branching (LCB) characteristics.

In many cases, SGIC in hyphenation with SEC via two-dimensional liquid chromatography (2D-LC) has proven to provide quantitative molar mass information about the eluting SGIC fractions. Such detailed 2D-LC analysis on the graft copolymers and TREF fractions was previously reported.²²

Triple Detection SEC Analysis of the Bulk Resins. For a comprehensive molar mass and branching investigation, the samples were further analyzed by using triple detection SEC (SEC-3D) that combines a concentration detector with an online viscometer and a light scattering detector.

The experimental procedure is provided in the [Supporting Information](#).

While SEC fractionates macromolecular chains according to hydrodynamic size, the use of specialized detectors such as an infrared detector (IRS) and a viscometer after the SEC column provides molar mass and branching information about the eluting fractions. To provide reliable quantitative information, the IRS detector was calibrated by using a series of ethylene–1-octene copolymers with a range of comonomer contents to determine the methyl contents of the SEC fractions as a function of molar mass. Average branching information determined by ¹³C NMR on the graft copolymers and TREF fractions were previously reported.²² Alternatively, analyzing the SEC fractions with an online viscometer provides information about molar mass (based on universal calibration), M_w and intrinsic viscosity, $[\eta]$. The absolute molar mass, M_{ab} , and the radius of gyration, R_g , are obtained by using a MALS detector. R_g and $[\eta]$ are influenced by both molar mass and molecular topology (branching). In solution, linear macromolecules exhibit extended coil conformations that are mainly influenced by molar mass. Accordingly, R_g and $[\eta]$ relate linearly to molar mass in accordance with the conformation and Mark–Houwink (MH) relationships in eqs 2 and 3, respectively.

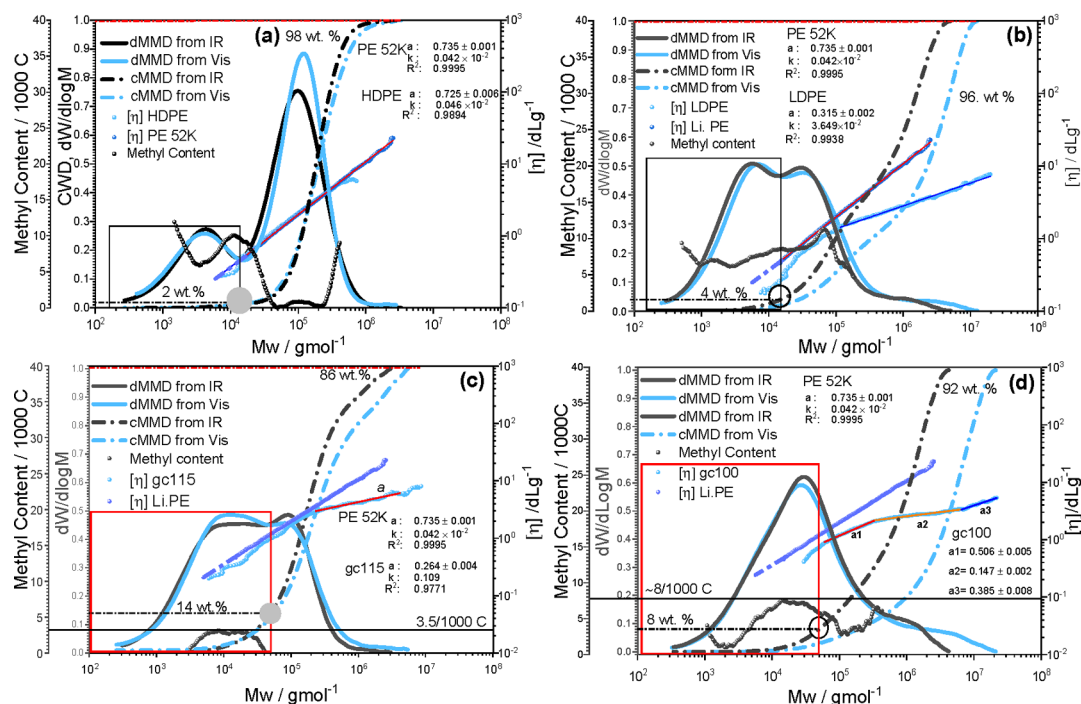


Figure 5. Superimposed MMD and Mark–Houwink plots of the homopolymers (a) HDPE and (b) LDPE comparing molar mass and branching characteristics to the graft copolymers (c) gc115 and (d) gc100. The Mark–Houwink plots of the analytes samples are compared to that of the PE 52K linear PE reference.

$$R_g = 0.029M_{ab}^{0.57} \quad (2)$$

$$[\eta] = 0.05M_v^{0.703} \quad (3)$$

For an ideal linear polymer such as linear polyethylene, the MH coefficients k (intercept) and α (slope) of the MH plot are 0.053 and 0.703, respectively.³⁵ These coefficients are 0.029 (k) and 0.570 (a) for the R_g to molar mass plot as proposed in the work of Wang et al.³⁸ Typically, LCB leads to significant coil size reduction resulting in decreasing R_g and $[\eta]$ compared to linear molecules. The degree of branching is characterized by a subsequent decrease in the slope of the MH plot of the branched polymer compared to a linear sample.

Figure 5 presents the differential and cumulative MMD curves along with the methyl concentration and MH distribution plots of the investigated samples as determined by IRS and Vis detectors. The cumulative MMD curve is obtained through the integration of the differential MMD curves. While the frequently used differential MMD (dMMD) curves easily reveal the molar mass of the most abundant fractions by displaying molar mass multimodality and symmetry distributions, the cumulative MMD curve (cMMD), allows for easy evaluation of the weight fractions and fraction amounts within a specified molar mass range. Figures 5a and 5b present plots of HDPE and LDPE, respectively. Both homopolymers display bimodal distributions indicating distinct molar mass populations with peak molar masses of around 4.2 and 120.6 kg/mol (HDPE) and 7 and 338 kg/mol (LDPE) based on universal calibration. The low molar mass fractions, which are highlighted in the black boxes, exhibit higher concentrations of methyl groups, suggesting a higher degree of branching. Based on the cMMD curves, the low molar mass, highly branched fractions constitute approximately 2 wt % (HDPE) and 4 wt % (LDPE) of the sample mass as indicated by the area under the black dashed

lines from the point the area touches the cMMD curves as indicated by the circles.

On the other hand, the high molar mass fractions, which constitute the plot areas of the cMMD curves between the black and red dashed lines, contribute approximately 98 wt % of HDPE and 96 wt % LDPE of their respective sample molar mass. As expected for HDPE, molecules within this molar mass region display no methyl content, admitting a linear structure. However, a sharp increase in methyl content is seen at the high molar mass region. In accordance with earlier work by Ewart et al., this is expected as the bis-biphenyl-phenoxy metallocene catalyst is known to incorporate small amounts of branches. This result concurs well with those of SSA and gradient HPLC.

In comparison, LDPE molecules within this high molar mass region display a higher concentration of methyl groups, confirming a more branched structure. For further confirmation, the MH plot of HDPE was compared to that of PE 52K (Li. PE). As is seen, the MH distribution plots of HDPE and PE 52K are superimposed and exhibit MH slopes of 0.725 and 0.735, respectively. These values are very close to 0.703 reported for an ideal PE reference, confirming a linear structure for HDPE. As expected for LDPE, a strong deviation of the MH plot away from that of the PE 52K toward lower $[\eta]$ is observed as molar mass increases. This behavior is typical for macromolecules with LCB, suggesting a branched topology for LDPE. These results agree well with those of gradient HPLC and SSA discussed earlier. The comparison of the SEC-3D data of HDPE and LDPE to those of the graft copolymers, gc115 and gc100 presented in Figures 5c and 5d, respectively, provide some interesting observations. First, gc115 displays a bimodal MMD curve with peak molar masses at 13 and 80 kg/mol, while gc100 exhibits a broad unimodal-like MMD curve with a peak molar mass of ~ 26 kg/mol and a shoulder at ~ 5060 kg/mol. Based on IRS measurements, a maximum methyl concentration of around 3.5/1000C is reported for the low

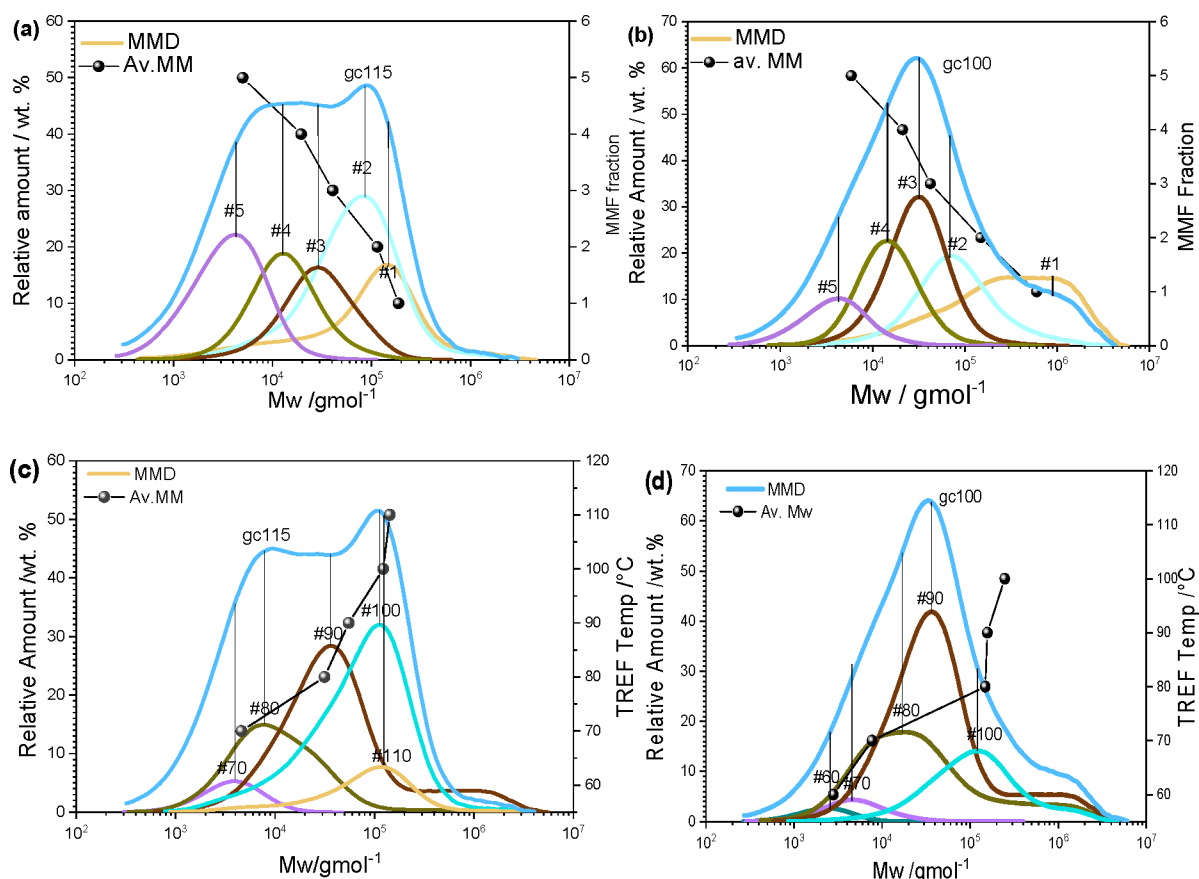


Figure 6. Superimposing MMDs plots of the MMF and TREF fractions of gc115 and gc100. The plots in (a) and (b) were generated by combining in (a) and (b) MMF \times SEC data and in (c) and (d) TREF \times SEC data. This combination converts the $dW/d \log M$ axis of a regular MMD plot to the relative amount in %.

molar mass fraction of gc115 in comparison to the 8/1000C observed for gc100 (see area highlighted in the red boxes), suggesting a higher level of branching for gc100. These branched but low molar mass fractions contribute 14 and 8 wt % of the sample molar mass of gc115 and gc100, respectively, as indicated by the areas of the cMMD curve under the black dashed lines. For LCB investigation of the graft copolymers, the MH plots were compared to that of PE 52K. At the low molar mass region, gc115 molecules display a linear MH plot, but at a lower intercept, which is a characteristic behavior of SCB. In comparison, a larger shift in the MH plot of gc100 to lower $[\eta]$ is seen which further confirms a higher level of branching for gc100. At the high molar mass region, the MH plots are seen to deviate increasingly from the linear plot as molar mass is increasing, a behavior typical of LCB. While the branched molecules of gc115 report a measured MH slope of 0.264, the MH plot of gc100 indicates a more complex architecture. To measure the slope, the plot was divided into three molar mass regions, and slopes a_1 (0.506), a_2 (0.147), and a_3 (0.385) were determined, suggesting a more complex architecture for gc100. These high molar mass, highly branched components of gc115 and gc100 contribute around 86 and 92 wt % of their respective sample molar masses.

Despite observing detailed microstructural information about the bulk resins by combining gradient HPLC with SSA and SEC-3D, it is still very challenging to distinguish the intrinsic properties of the graft copolymer chains from those of linear and branched homopolymers. For a comprehensive evaluation of the molecular structure of these polymers, the

samples were fractionated preparatively followed by analyses of the fractions.

Preparative Fractionations and Fraction Analyses. In the next experimental step, the bulk resins were fractionated by pMMF and pTREF to generate “well-defined” library fractions with relatively narrow molar mass and chemical composition distributions, respectively. Detailed information about the pTREF process and the analysis of the fractions was previously published.²² The current work focuses on the pMMF process and the analysis of the pMMF fractions along with the discussion of pTREF results. The MMD curves in Figure 6 illustrate the relative amounts of each MMF/TREF fraction as a function of molar mass and molar mass distributions of the bulk samples as well as the MMF/TREF fractions. Quantitative information about the fractionation processes and the molar mass parameters are presented in Table S2.

The MMD curves of the MMF fractions of gc115 and gc100 are given in Figure 6a and 6b, respectively. Similar plots of the MMF fractions of HDPE and LDPE are provided in Figures S1a and S1b. Except for the MMF fractions #1 that show very broad MMDs with molar mass dispersities of 10.7 and 10.1, respectively, the other fractions display relatively narrow unimodal MMDs with molar mass dispersities ranging between 1.9 and 4. MMF fractions #1 and #2 jointly contribute approximately 48.4 and 45.9 wt % of the total mass of gc115 and gc100, respectively. These two fractions constitute the higher molar mass components and exhibit average molar masses above 100 kg/mol. The higher MMF fractions (i.e., #3 to #5) exhibit average molar masses below 45 kg/mol and

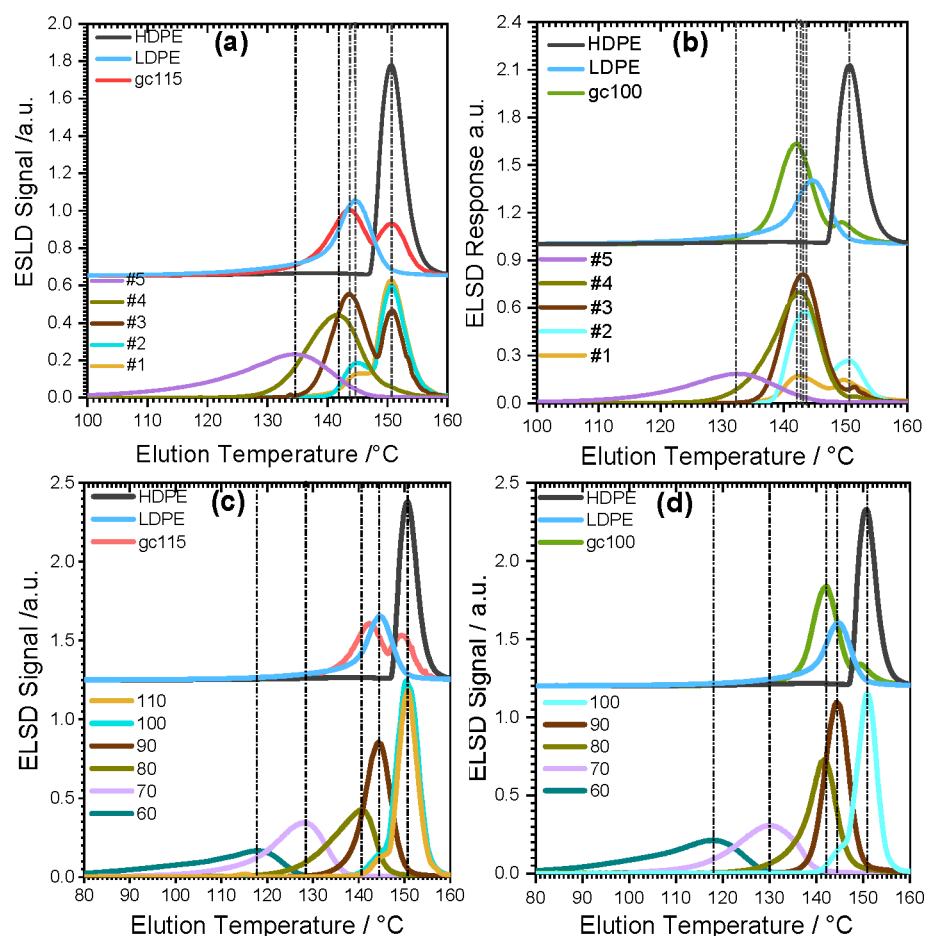


Figure 7. TGIC elugrams of MMF/TREF fractions of gc115 (a, c) and gc100 (b, d) collected at a solvent flow of 0.5 mL/min and a temperature ramp of 4 °C/min using PGC and *o*-DCB as stationary and mobile phases, respectively.

jointly make up 51.6 and 54.1 wt % of gc115 and gc100, respectively. In general, the MMF fractions show a linear increase in the weight-average molar masses with decreasing fractionation number. Similar plots of the TREF fractions of gc115 and gc100 are provided in Figures 6c and 6d, respectively.²⁵ Because of limited amounts of the 30, 60, 110, and 130 °C fractions, PE equivalent molar mass data were not determined. Polystyrene equivalent molar mass information about all the TREF fractions was previously reported.²² As expected, the TREF fractions have increasing molar masses with increasing TREF elution temperatures. Except for the 90 °C fractions that display molar mass bimodalities, all other fractions display monomodal MMD curves. Molar mass dispersities ranging between 1.6 and 14 were recorded, suggesting significant molar mass heterogeneities in some fractions. From the relative amounts of the fractions, it is clear that the 90 and 100 °C fractions are the principal components of gc100 and gc115, respectively, with each making up 48 and 34 wt % of the total sample mass, respectively.

Generally, an increase in the fraction molar masses is seen with an increase in the fractionation temperatures. This behavior differs greatly from the behavior of commercial LDPE, where almost constant peak molar masses were recorded for the majority of TREF fractions.²⁵ To acquire information regarding the chemical composition/branching distributions, the fractions were analyzed by TGIC using *o*-DCB as the isocratic mobile phase. The elugrams in Figures 7a and 7b represent TGIC plots of MMF fractions of gc115 and

gc100, respectively. Fractions #1 and #2 of sample gc115 exhibit bimodal elution profiles with peak elution temperatures at 150.6 and 144.8 °C, suggesting a chemical composition/branching heterogeneity. By comparison of the elution peaks to those of the bulk resins HDPE and LDPE, it is evident that the higher temperature elution peak corresponds to HDPE, suggesting a majority of linear PE chains.

The lower temperature peak corresponds to LDPE elution behavior, indicating a small amount of high molar mass, highly branched PE chains coprecipitating in pMMF with the high molar mass linear components.

In contrast, the pMMF fractions #4 and #5 elute at temperatures that are close to LDPE and, accordingly, can be assigned to highly branched PE structures. Of particular interest is the elugram of fraction #3, which exhibits a bimodal profile with peaks maxima at 150.8 and 143.7 °C.

While the former peak can be assigned to linear PE, the latter peak is due to PE chains with an increased level of branching. By integrating the different peak areas of gc115 and combining peak areas of PE chains with similar elution temperatures, it is found that ~45 wt % of the fractions exhibit linear characteristics and ~55 wt % are due to branched macromolecules. Similar plots of pMMF fractions are presented in Figure 6b for sample gc100.

In this case, however, the majority of all fractions elute at temperatures that are characteristic for branched molecules while only small amounts of material elute at about 150 °C, which are typical for linear structures. The combination of

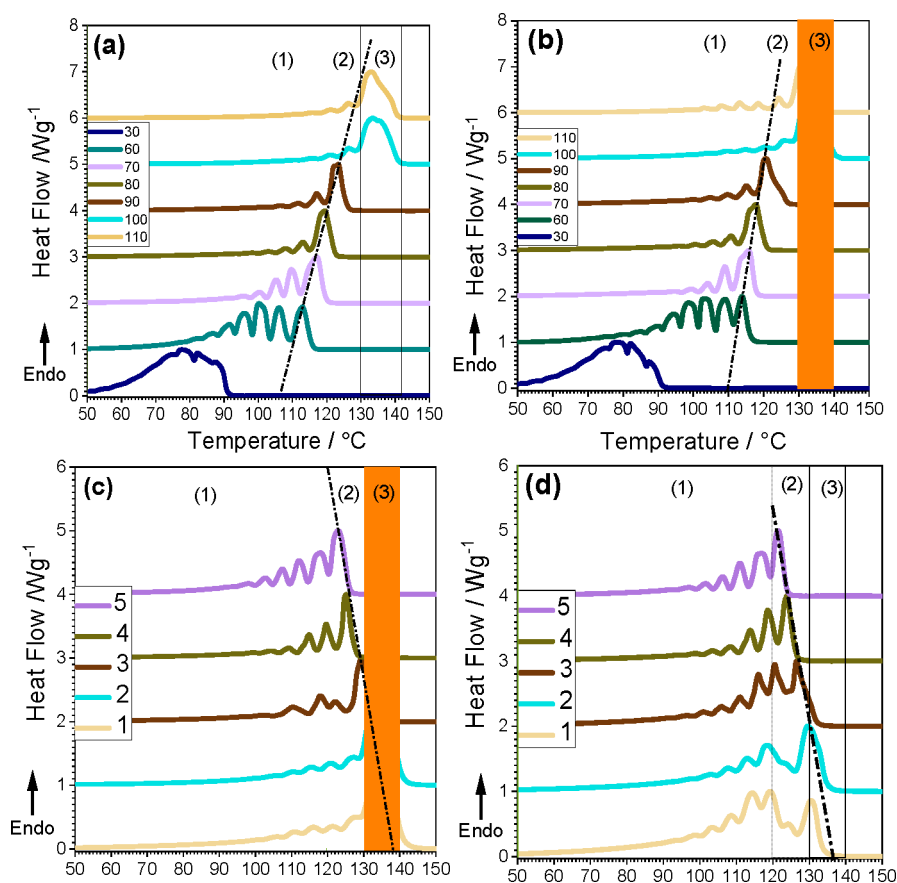


Figure 8. Plots of SSA melting endotherms of TREF fractions (a, b) and MMF fractions (c, d) for gc115 (a, c) and gc100 (b, d). Three temperature regions (1–3) are defined and discussed in the text.

peaks with similar elution characteristics shows that ~ 82 wt % of gc100 are branched structures, suggesting a higher level of total branching.

HPLC Analysis of Preparative Fractions. In the next step of this study, the compositional heterogeneity of the TREF fractions was investigated by TGIC. Chromatograms of the individual fractions of gc115 and gc100 are presented in Figures 7c and 7d, respectively.

Except for the 110 and 100 °C fractions, monomodal elution profiles are observed.

Generally, it is found that the peak elution temperatures decrease with decreasing TREF fractionation temperatures. These results agree well with the TREF principle, which is known to generate narrowly dispersed branched fractions with a decreasing level of branching as TREF temperatures increase. The observed increase in peak broadening is suggesting chains with increasing chemical composition heterogeneity. On the other hand, this might be an indication of an increasing molar mass effect since most of the low temperature fractions have molar masses below 20 kg/mol. The comparison of the fractions with the HDPE precursor indicates that the 100 and 110 °C TREF fractions consist of predominantly linear PE chains. Details of the SGIC analysis of the TREF fractions were previously reported,²² while SGIC plots and the analysis of the MMF fractions are presented in Figure S2.

As has been shown, both solvent and temperature gradient interaction chromatography are capable of separating branched from the linear PE chains. Accordingly, the amount of non-grafted HDPE backbone can be determined.

The more important challenge is the separation of the LDPE grafts that are not attached to HDPE from the true graft copolymers HDPE-*g*-LDPE. This challenge shall be addressed by SSA experiments assuming that the heat of fusion and the melting point of molecules with differences in molecular structure/topology differ significantly due to differences in the crystal sizes formed. The following section is aimed at exploiting these structural differences by segregating the grafted copolymer chains and the non-grafted LDPE chains. In this new set of experiments, the preparative fractions are analyzed by SSA, a fractionation method that segregates semicrystalline polymer chains based on their crystallizable methylene sequence length (MSL). The SSA plots of the TREF fractions of gc115 and gc100 are presented in Figures 8a and 8b, respectively. Each fraction displays a melt endotherm with multiple seeds, suggesting distributions in the lengths of crystallizable units. A summary of the thermophysical properties and T_s temperatures of each fraction is provided in Table S3. In line with TREF principles, the peak melting temperatures of the principal seeds increase with an increase in the fractionation temperature.

SSA Analysis of Preparative Fractions. For convenient interpretation of the results in Figure 8, the plot area is divided into three temperature regions labeled 1–3. Based on earlier assignments, melting events within region 1 are due to either LDPE chains or graft copolymer chains with a high level of branching/grafting. On the other hand, the melting events within the regions labeled 2 and 3 are ascribed to the graft copolymer and HDPE chains, respectively. A close inspection

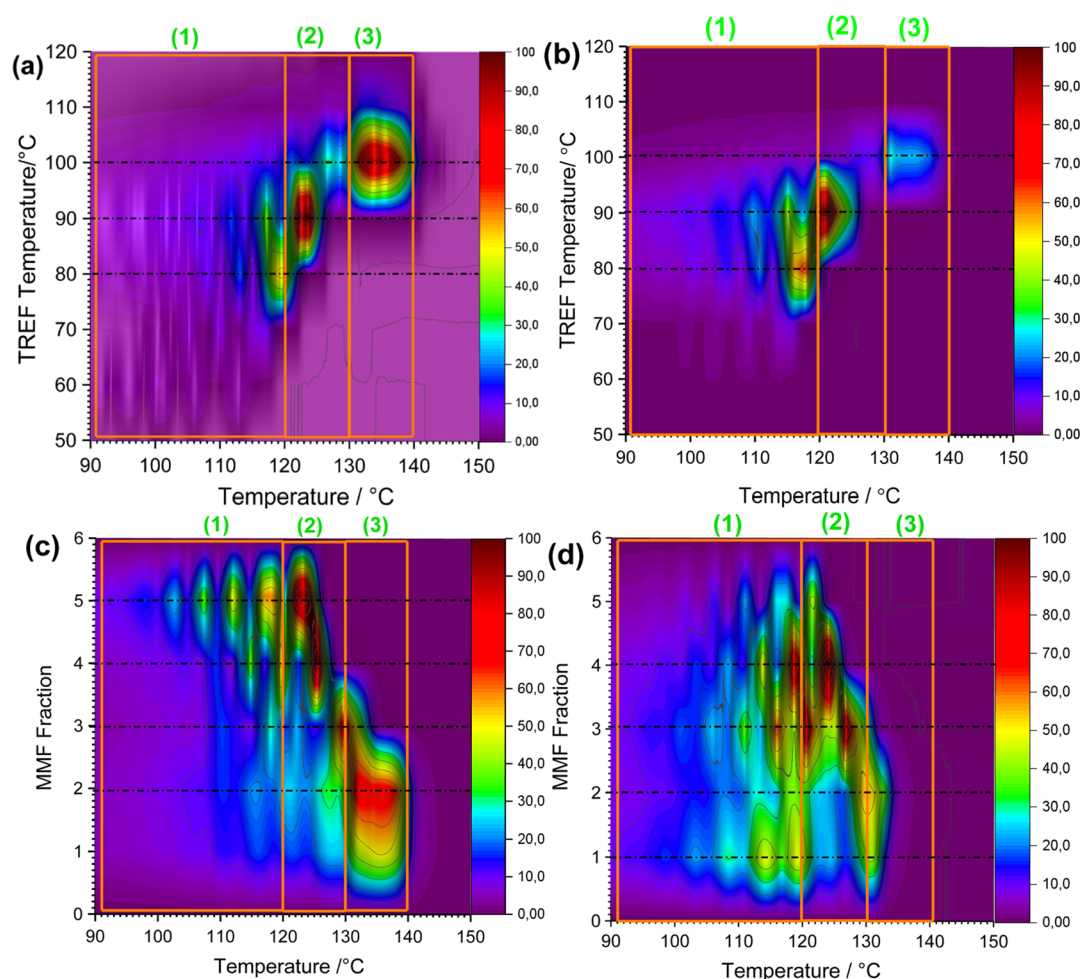


Figure 9. Two-dimensional (2D) contour plots obtained by combining TREF \times SEC (a, b) and MMF \times SEC data (c, d). These plots combine melting events of SSA seeds of gc115 (a, c) and gc100 (b, d). Three temperature regions (1–3) are defined and discussed in the text.

of the plots of gc115 and gc100 reveals that the 30–80 °C TREF fractions exhibit melting within region 1 and may constitute mainly LDPE.

In contrast, the 100 and 110 °C fractions show melting events within region 3, which are associated with the HDPE homopolymer chains. Most importantly, the melting events of the main seeds are broad and display shoulders at higher temperatures, indicating a mixture of molecules with different melting temperatures and, therefore, distinct chemical structures.

Of particular interest are the melting events of the main seed of the 90 °C fractions, which are seeds within zone 2 and may constitute mainly the graft copolymer chains. Based on these findings, TREF fractions mainly consisting of HDPE, LDPE, and the graft copolymer chains of gc115 and gc100 were identified. Similar SSA plots of the MMF fractions of gc115 and gc100 are presented in Figures 8c and 8d, respectively. The presence of melting events with multiple peaks is suggesting chemical composition heterogeneity of the fractions. As indicated by the dotted line, the peak melting temperatures of the main seeds decreases linearly with increasing MMF fraction number or decreasing fraction molar mass. This behavior contradicts previous findings on MMF fractions of commercial LDPE, where more constant peak melting temperatures were observed. These differences

may align well with differences in the broad molar mass and chemical composition heterogeneities of the current samples.

According to the assigned temperature regions, it is seen that the main components of gc115 fractions 1 and 2 show melting events within region 3, which is typical of HDPE chains. However, the main seeds of similar fractions of gc100 display melting events midway between region 2 and 3 with peak melting temperatures around 130 °C. This behavior is typical of HDPE chains with a low level of branching/grafting. More interestingly, the peak temperatures of the main seeds of fractions 3 to 5 of gc115 and gc100, which display melting events within region 2, suggest a dominant presence of graft copolymer chains.

To correlate the melting events of the seeds to molar mass/crystallizability, comprehensive two-dimensional (2D) plots are constructed by combining pMMF/pTREF and SSA data as shown in Figure 9. According to the 2D contour plots of the TREF fractions of gc115 and gc100 shown in Figure 9a and 9b, respectively, three baseline separated crystal size regimes are identified at 80, 90, and 100 °C TREF temperatures (see black dashed lines). The crystal size regimes are seen to display melting events within the temperature regions 1, 2 and 3, respectively. While the regimes at 100 and 80 °C are mainly associated with the HDPE and LDPE homopolymer chains, respectively, the regime at 90 °C TREF temperature constitutes mainly the graft copolymer chains.

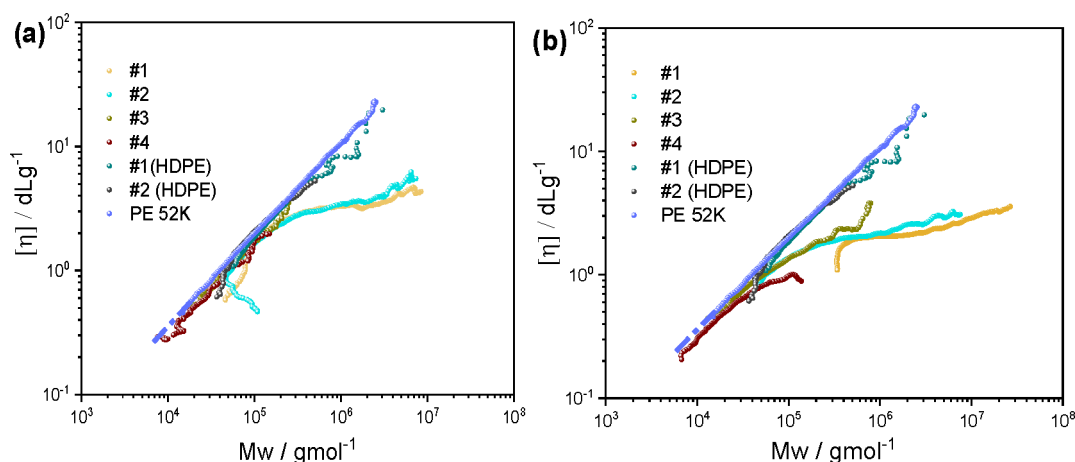


Figure 10. Mark–Houwink plots comparing LCB branching characteristics between fractions of (a) gc115 and (b) gc100 as determined by SEC-vis measurements. Data of fraction 5 showing low molar mass were omitted.

In addition, the regimes at 100 °C display bimodal crystal size distributions, showing a smaller amount of polymer chains melting within zone 2, admitting the presence of graft copolymer chains. In general, the main component of gc115 is observed at 100 °C TREF temperature, while the regime at 90 °C TREF temperature is the main component of gc100, suggesting a higher level of grafting in gc100. In comparison, the 2D contour plots of the MMF fractions of gc115 and gc100 display four crystal size regimes at MMF dashed lines in Figure 9c and 9d, respectively, indicating molar mass heterogeneity.

While the high molar mass components (fractions 1 and 2) of gc115 show melting events within region 3, suggesting a dominant presence of HDPE macromolecules, the melting events of similar fractions of gc100 are distributed between regions 1 and 3, indicating a coprecipitation of high molar mass HDPE and LDPE macromolecules. Also, the mid molar mass fractions (3 and 4) of gc115 exhibit melting events within region 2, indicating the presence of graft copolymer chains.

The melting events for similar fractions of gc100 are distributed between regions 1 and 2, suggesting the coprecipitation of LDPE and graft copolymer macromolecules. However, the major low molar mass component (fraction 5) of gc115 is seen predominantly within zone 2, while the major component of a similar fraction of gc100 is equally distributed between zones 1 and 2, suggesting a more complex composition in gc100. From these findings, it can be concluded that the higher molar mass components of gc115 constitute predominantly HDPE macromolecules, while the graft copolymer chains are mainly of medium molar masses. On the other hand, the components of gc100 are distributed across all molar mass ranges, admitting a more complex mixture of graft copolymer and LDPE chains in gc100.

SEC Analysis of the Preparative Fractions. To fully understand the intrinsic properties of the different components, it is imperative to link the melting and elution behaviors obtained from SSA and HPLC to the branching structure.

The MH distribution plots of the fractions of gc115 and gc100 are compared first to PE 52K, #1 and #2 of HDPE and last with each other, as shown in Figures 10a and 10b, respectively.

The MH plots of #1 and #2 of HDPE show linear behavior at the mid-molar mass region and deviate slightly at a higher molar mass, indicating some branching structure. This behavior is not surprising since the catalyst used is known to

incorporate macromers on the growing chains.^{20,21} Plots showing the methyl content distributions are provided in Figure S3.

As is seen, gc115 fractions 3 and 4 display linear MH plots at lower intercepts, a characteristic behavior of macromolecules with SCB. The melting events of the main seeds of these fractions are seen within region 2 and may be assigned to the graft copolymer chains. The complete absence of LCB in these fractions indicates the absence of HDPE-*g*-LDPE chains as well as LDPE with LCBs. However, macromolecules with such unique characteristics may be attributed to either HDPE-*block*-LDPE copolymer chains (HDPE-*b*-LDPE) or LDPE chains with predominantly SCB. As described in the proposed reaction scheme (see Figure 2), the block copolymers chains may either be formed by the combination of a HDPE (6) and a LDPE primary radical (4) or by the propagation of the HDPE primary radical (6) to HDPE-*b*-LDPE copolymers assigned as products (10) and (9). These products may contain predominantly SCB. On the other hand, fractions 1 and 2 deviate strongly from the plot of PE 52K, indicating macromolecules with LCB. The stronger deviation of fraction 1 at the higher molar mass region is indicative of a higher level of LCB.

Although these fractions show LCB characteristics, it is important to note that their melting events were recorded within region 3 assigned to HDPE macromolecules. Such a unique characteristic which combines the HDPE melting temperature and the LDPE high LCB can be associated with the graft copolymer chains formed by grafting LDPE onto HDPE backbone assigned as product (8) in Figure 2. Similar MH plots of the TREF fractions were previously reported, and the highly crystalline fractions (100 and 110 °C fractions) that display melting temperatures above 130 °C also exhibit LCB characteristics.²²

In the case of gc100 (see Figure 10b), the MH plots of all the fractions deviate from the linear plot, confirming the presence of LCB. In addition, a stronger deviation is seen with decreasing fraction number or increasing fraction molar mass. While fraction 2 displays LCB behavior and exhibits melting mostly within regions 2 and 3 indicating HDPE-*g*-LDPE copolymer chains, fraction 1, on the other hand, displays bimodal melting behavior: first within region 1, indicating LDPE chains, and second between regions 2 and 3, which are assigned to the grafted copolymer chains. Both fractions 3 and

4 show LCB behavior, and the melting events of their main SSA seed were observed within region 2, indicating a dominant presence of grafted copolymer chains with a higher degree of LCB branching. From these findings, it is concluded that gc100 constitutes a mixture of predominantly graft copolymer chains with a small amount of LDPE, while gc115 constitutes a mixture of graft and block copolymer species.

CONCLUSION

In this study, the molecular complexity of graft copolymers HDPE-g-LDPE was investigated. These polymers were produced from supercritical ethylene by using a dual reactor setup. In the first step of the polymerization, HDPE was produced that was grafted with LDPE in the second step. On the basis of the different possible polymerization pathways it was proposed that several different polymer species were present in the final product mixture, including the “precursor” homopolymers (HDPE and LDPE), the graft copolymer HDPE-g-LDPE, and some block copolymer species HDPE-*b*-LDPE.

The molecular structure of the bulk samples was investigated by using gradient HPLC (SGIC and TGIC) in combination with SSA and SEC-3D. The gradient HPLC profiles of the grafting products were compared to their LDPE and HDPE counterparts and macromolecules with branched and linear structures were identified. Because of the coelution effect in HPLC analysis, it was very challenging to separate the graft copolymer molecules from the homopolymers. A similar challenge was observed with the CRYSTAF and TREF analysis previously reported due to the cocrystallization effect.

The samples were further investigated by SSA to correlate the heat of fusion and melting behavior to the different polymer species. The results revealed the presence of polymer species with melting characteristics comparable to HDPE and LDPE. In addition, these precursor polymers and macromolecules with melting behaviors typical of branched polyethylene were identified and were attributed to the graft copolymer species.

The samples were then analyzed with SEC-3D to observe LCB characteristics of the different polymer species. Mark-Houwink plots of all species were compared to plots of linear reference PE. While LDPE and HDPE show MH plots typical of branched and linear macromolecules, the MH distribution plots of the graft copolymer samples were more complex and indicated mixtures of components with branched and linear characteristics.

For a comprehensive investigation, the samples were subjected to preparative fractionation using the multiple preparative fractionation protocol. Fractions with varying molar masses were obtained via pMMF, while fractions with varying degrees of branching were obtained via pTREF. Analysis of the fractions by HPLC and SSA indicated that the high molar mass/higher crystalline fractions constitute mainly the HDPE macromolecules with small amounts of graft copolymer/LDPE. On the other hand, the mid-to-low elution temperature TREF fractions and the mid-to-low molar mass MMF fractions indicated the presence of grafted/branched macromolecules.

Analysis by SEC-3D revealed that the high molar mass fractions of gc115 showing melting characteristics typical of HDPE exhibit MH plots typical of branched macromolecules. This unique behavior that combines the high melting of HDPE and the LCB behavior of LDPE is attributed to HDPE-g-LDPE

macromolecules. On the other hand, mid-molar mass fractions displayed linear MH plots typical of polymers with SCB and thus exhibit melting typically of ethylene copolymers. This combined characteristic was assigned to copolymer chains with block structures such as HDPE-*b*-LDPE. All the fractions of sample gc100 displayed branched characteristics and showed melting behaviors typical of the graft copolymer species.

On the basis of the current analysis, it is concluded that the grafting reaction is enhanced by decreasing the temperature in the tube reactor (second polymerization step). However, this hypothesis may require further investigations. In summary, to conduct a comprehensive analysis of such complex polyolefins, it is imperative to apply the multiple preparative fractionation concept and to combine this with a range of advanced analytical methods.

The production of HDPE-g-LDPE copolymer could be of great industrial benefit as the stiffness of HDPE can be combined with the processability of LDPE in a single product.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsapm.0c01094>.

- (1) Experimental procedures for SEC, SSA, pMMF, pTREF, ethylene polymerization, and grafting,
- (2) SGIC analysis of pMMF fractions,
- (3) molar masses of preparative fractions, and
- (4) thermophysical properties of fractions obtained by DSC and SSA (PDF)

AUTHOR INFORMATION

Corresponding Author

Harald Pasch – Department of Chemistry and Polymer Science, University of Stellenbosch, 7602 Stellenbosch, South Africa; orcid.org/0000-0003-1132-3393; Email: hpasch@sun.ac.za

Authors

Paul S. Eselem Bungu – Department of Chemistry and Polymer Science, University of Stellenbosch, 7602 Stellenbosch, South Africa; orcid.org/0000-0002-4798-5850

Kristina Zentel – Technical Chemistry III, Technical University Darmstadt, 64287 Darmstadt, Germany; orcid.org/0000-0001-6209-539X

Sascha Hintenlang – Technical Chemistry III, Technical University Darmstadt, 64287 Darmstadt, Germany

Markus Busch – Technical Chemistry III, Technical University Darmstadt, 64287 Darmstadt, Germany

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acsapm.0c01094>

Author Contributions

M.B. and H.P. contributed equally to this work.

Notes

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■ ABBREVIATIONS

MAAO, modified methylaluminoxane; TBPA, *tert*-butylperoxy acetate.

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