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# Fractionation of Ethylene/1-Octene Copolymers by High-Temperature Thermal Gradient Interaction Chromatography

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**ABSTRACT:** High-temperature thermal gradient interaction chromatography (HT-TGIC) was recently introduced into the area of polyolefin analysis. This new technique uses commercially available Hybcarb columns to separate polyolefin chains based on their interaction with the porous graphitic carbon stationary phase in a temperature gradient mode. In this paper, a systematic study of HT-TGIC operation conditions is presented for ethylene/1-octene copolymers and their blends. One of the objectives of this investigation is to identify the best set of conditions that maximize peak separation of copolymers in a binary blend. Although the chromatograms of individual resins and their blends are independent of the cooling rate, it will be shown that sample volume (column loading) and heating rate during the elution cycle affect the peak separation of the components in binary blends.

## 1. INTRODUCTION

Ethylene/ $\alpha$ -olefin copolymers can be used in many different applications because their properties can be tuned by changing their crystallizability via comonomer incorporation. Therefore, the characterization of comonomer composition distribution (CCD) in olefin copolymers is of great importance in industrial and academic investigations. Traditionally, the CCDs of ethylene copolymers have been characterized using solution crystallization-based methods. Temperature rising elution fractionation (TREF) and crystallization analysis fractionation (CRYSTAF) have been used for characterization of the CCD of polyolefins since the eighties and nineties, respectively. A newer crystallization-based technique, crystallization elution fractionation (CEF), has been invented by the research group at Polymer Char to enhance the resolution of TREF and CRYSTAF and to shorten analysis time. However, these techniques cannot be used to fractionate polyolefins with lower crystallizabilities (or amorphous polyolefins) because they do not crystallize from a dilute solution. High-temperature high-performance liquid chromatography (HPLC), on the other hand, can extend the range of CCDs that can be measured by crystallization-based techniques.

Although polyolefins have been produced industrially for more than 70 years, the characterization of polyolefins based on their chemical composition by HPLC was unknown until recent years. Before 2003, the use of the HPLC was limited to ambient or slightly elevated temperature (up to 80 °C).<sup>1,2</sup> In 2003, Macko et al.<sup>3,4</sup> reported that HPLC could be used in a precipitation-redissolution mechanism to separate isotactic polypropylene from linear polyethylene using ethylene glycol monobutylether (EGMBE) as eluent. The HPLC column used in their experiments was packed with silica gel chemically modified with oligo(dimethylsiloxane).<sup>5,6</sup> The separation of isotactic polypropylene from polyethylene in this system relied on the fact that EGMBE is a good solvent for polypropylene but a nonsolvent for polyethylene.<sup>7</sup> The main difficulty with this method is that the polyethylene recovery decreases as the

molecular weight increases. In addition, this method has poor resolution and is limited by the poor solubility of polyolefins. To overcome these limitations, Heinz and Pasch<sup>8</sup> used a gradient of trichlorobenzene (TCB, a good solvent for both polyethylene and polypropylene). The polymer sample was dissolved in 1-decanol and injected into a HPLC column packed with modified silica gel. The mobile phase was then started with 100% EGMBE for 2 min. During this short period of time, polypropylene was separated from the blend, while polyethylene precipitated on the column packing. The volume fraction of TCB was then increased linearly to 100% within 3 min, and kept constant for about another 3 min. The column outlet was connected to an evaporative light scattering detector.

The pioneering work of Macko and Pasch<sup>9–11</sup> opened the route to characterize polyolefins using high-temperature HPLC based on the adsorption–desorption mechanism. The use of Hypercarb porous graphitic carbon packing was the key for the recent successful characterization of polyolefins with this technique. Polyethylene, ethylene/ $\alpha$ -olefin copolymers, atactic polypropylene, and syndiotactic polypropylene were fully adsorbed on Hypercarb columns at 160 °C. The retained polymers were desorbed and eluted from the column using a solvent gradient from 100% 1-decanol to 100% TCB.<sup>9–12</sup> HPCL was also used as a component in two-dimensional liquid chromatography: Ginsburg et al.<sup>13,14</sup> and Roy et al.<sup>15,16</sup> have combined HPLC and high-temperature gel permeation chromatography instruments to analyze a blend of isotactic polypropylene, atactic polypropylene, syndiotactic polypropylene, and polyethylene.

These methods (either one or two-dimensional HPLC-based techniques) need a solvent gradient to perform the separation.

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However, the adsorption of polymer chains on a substrate also depends on temperature. Based on this fact, Lochmüller<sup>17</sup> and Chang<sup>18</sup> were able to separate polyethylene glycol and polystyrene, respectively, using temperature gradient adsorption HPLC. During the Third International Conference on Polyolefin Characterization, Cong et al.<sup>19</sup> showed for the first time that temperature gradient adsorption HPLC can be utilized for polyolefin fractionation using a Hypercarb column. This method (HT-TGIC) opens a new route to quickly characterize crystalline and amorphous polyolefins. In addition to its simpler operation (it does not require the use of a solvent gradient), the use of a single solvent permits the use of quantitative mass detectors such as infrared detectors, eliminating the need to rely on nonquantitative evaporative light scattering detectors. In HT-TGIC, the polymer is dissolved in a good solvent, such as *o*-dichlorobenzene, and injected into a Hypercarb column at high temperature. HT-TGIC is similar to TREF and CEF in that it needs two temperature cycles: cooling to adsorb the polymer chains onto the porous graphite support and heating to desorb and elute the retained fractions from the column using a constant solvent flow rate. Cong et al. have used HT-TGIC to fractionate a series of ethylene/1-octene copolymers. They found that the peak temperatures of the HT-TGIC chromatograms correlated linearly with 1-octene content in the copolymer samples.<sup>19</sup> Monrabal et al.<sup>20</sup> claimed that the dependence of HT-TGIC elution peaks on the molar mass of polymer was insignificant for samples with molar masses above 25 kg/mol. Moreover, they combined TGIC and CEF to form a cross-fractionation instrument with enhanced peak separation. It has also been reported that other support types such as molybdenum sulfide, boron nitride, and tungsten sulfide can also be used to fractionate polyolefins by HT-TGIC.<sup>21</sup>

In this investigation, a systematic study of HT-TGIC of ethylene/1-octene copolymers and their blends was conducted to provide a more detailed understanding of the factors that influence the separation process in HT-TGIC. This understanding is essential for the quantification of HT-TGIC and estimation of CCD of polyolefins using this technique. The effect of operating conditions such as cooling rate, heating rate, adsorption/desorption temperature range, and sample volume were studied carefully to find out the best set of conditions that enhanced the resolution of HT-TGIC.

## 2. EXPERIMENTAL SECTION

All the HT-TGIC experiments were performed using the crystallization elution fractionation (CEF) instrument (Polymer Char, Valencia, Spain), by replacing the original CEF column with a Hypercarb column. The instrument consists of an autosampler, a programmable column temperature oven, an isocratic pump, and an infrared detector. The polymer samples were first dissolved in 8 mL of solvent in 10 mL vials. The dissolution was carried out in the instrument's autosampler at 160 °C. The dissolution time was 1 h. All the experiments in this study were performed using ODCB as a solvent. Antioxidant (Irganox 1010) was added to the solvent at a concentration of 0.25 g/L to protect the sample from thermal degradation during the analysis. The sample concentrations were 1 mg/mL for the individual resins and 2 mg/mL when two resins were blended. Each sample was loaded into the column at a temperature of 155 °C. The sample was kept at the front of the column for 5 min to stabilize its temperature. Increasing the stabilization time to 30 min did not affect the

obtained chromatograms. After the stabilization, the column temperature was reduced gradually to allow the polymer chains to adsorb onto the porous graphitic carbon material inside the column under a small solvent flow ("CEF mode"). At the end of the cooling cycle, the temperature of the column was kept constant at the final cooling temperature for 3 min. Then, the pump flow rate was increased to the desired elution flow rate to remove the soluble fraction that was not adsorbed at the final cooling temperature. The temperature was then increased at a certain heating rate to desorb and elute the retained polymers. An IR4 infrared detector (from Polymer Char, Valencia, Spain) was integrated into the instrument and was used in all the HT-TGIC analyses. The experiments were performed using a Hypercarb column (10 cm long and 4.6 mm internal diameter, from Thermo Scientific).

The average properties of the polyethylene and ethylene/1-octene copolymers analyzed in this investigation are listed in Table 1. The samples have different 1-octene molar fractions

**Table 1. Ethylene/1-Octene Samples**

sample	octene (mol %)	$M_n$
m-1	0	46 600
m-2	0.16	48 161
m-3	1.16	47 000
m-4	2.2	47 700
m-5	3.51	49 800

but about the same number average molecular weights; all samples have a polydispersity index of about 2.0. The observed effects are, consequently, correlated to the fraction of 1-octene in the copolymers and not to their molecular weights. In addition, three 50/50 wt % blends were used in this study to test the separation resolution by HT-TGIC. The components of these blends are listed in Table 2. All polymer samples were kindly donated by Dow Chemical.

**Table 2. Blend Components**

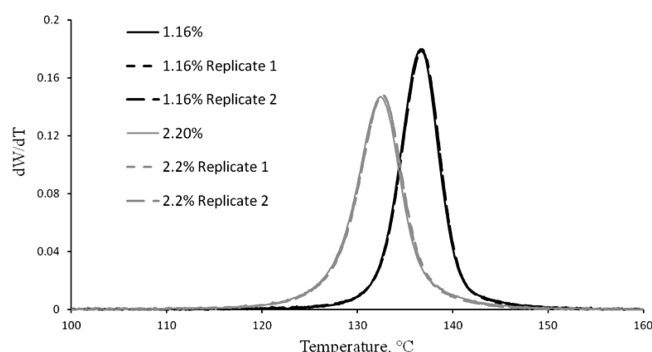
sample	component 1	component 2
blend-1	m-4	m-3
blend-2	m-5	m-3
blend-3	m-5	m-2

## 3. RESULTS AND DISCUSSION

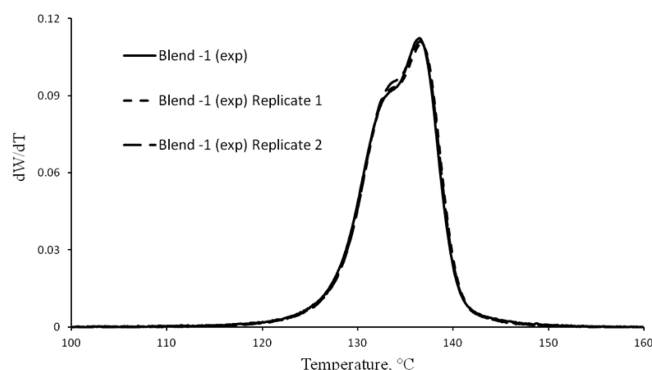
Table 3 lists the main parameters studied in this work. The reproducibility of the HT-TGIC chromatograms was excellent, as illustrated in Figure 1 for some of the individual samples and in Figure 2 for Blend-1. The analysis of two individual resins, m-3 (1.16 mol % octene) and m-4 (2.2 mol % 1-octene) and their 50/50 wt-% blend (Blend-1) was repeated three times

**Table 3. Main Operating Conditions**

parameter	symbol	values
cooling rate (°C/min)	CR	1; 5
cooling cycle range (°C)		155–35; 155–90
cooling flow rate (mL/min)	Fc	0; 0.01; 0.02
heating rate (°C/min)	HR	1; 3
elution flow rate (mL/min)	Fe	0.5
sample size (μL)	SZ	50; 100; 400



**Figure 1.** Repeatability of HT-TGIC profiles for individual resins. Experimental conditions: SZ = 400  $\mu$ L, CR = 5  $^{\circ}$ C/min (155–90  $^{\circ}$ C), Fc = 0.02 mL/min, HR = 1  $^{\circ}$ C/min (90–160  $^{\circ}$ C), Fe = 0.5 mL/min.

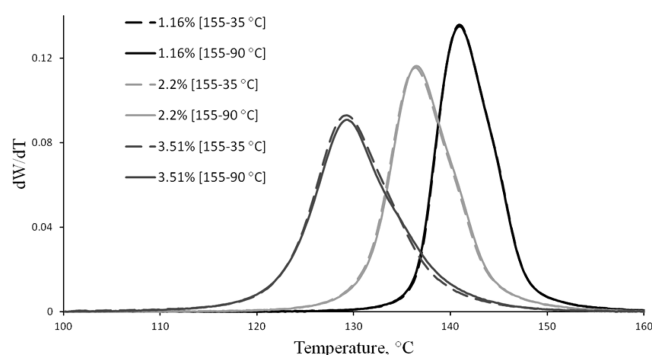


**Figure 2.** Repeatability of HT-TGIC profiles for blend-1. Experimental conditions: SZ = 400  $\mu$ L, CR = 5  $^{\circ}$ C/min (155–90  $^{\circ}$ C), Fc = 0.02 mL/min, HR = 1  $^{\circ}$ C/min (90–160  $^{\circ}$ C), Fe = 0.5 mL/min.

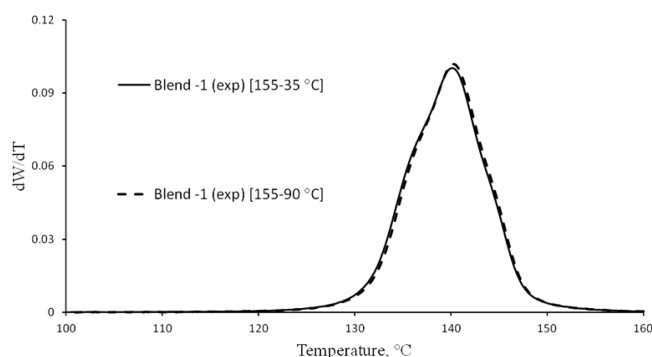
using a cooling rate of 5  $^{\circ}$ C/min, a heating rate of 1  $^{\circ}$ C/min and elution flow rate of 0.5 mL/min.

**3.1. Effect of Adsorption/Desorption Temperature Range.** Similarly to TREF and CEF, HT-TGIC analyses require two temperature cycles: cooling and heating. In the cooling cycle, the adsorption of the polymer chains on the porous graphitic carbon material takes while the column temperature is decreasing. For ethylene/ $\alpha$ -olefin copolymers, the fraction with the lowest  $\alpha$ -olefin comonomer content is adsorbed first at the highest temperature, whereas the other fractions remain in the solvent phase until their adsorption temperatures are reached. In the heating cycle, the retained polymer chains are eluted with the solvent at increasing temperatures. The solvent first removes the fractions with higher comonomer content followed by those with lower comonomer content. The fraction process resembles that of TREF and CEF, except that it is governed by chain adsorption, not chain crystallization. Crystallization may, however, occur after adsorption if the column temperature is lowered below the crystallization temperature of the polymer chains. For the samples investigated herein, crystallization does not seem to have any significant role in the fractionation.

Two adsorption/desorption temperature ranges were studied for the individual resins and their blends. In both sets of experiments, the polymer samples were injected in the column at 155  $^{\circ}$ C. Then, the column temperature was decreased either to 35  $^{\circ}$ C or to 90  $^{\circ}$ C. During the heating cycle, the column temperature was increased to 160  $^{\circ}$ C. The HT-TGIC profiles using these two temperature ranges are shown in Figures 3 and 4 for three individual resins and blend-1, respectively. The



**Figure 3.** Effect of adsorption/desorption temperature range on HT-TGIC profiles for individual resins. Experimental conditions: SZ = 400  $\mu$ L, CR = 5  $^{\circ}$ C/min, HR = 3  $^{\circ}$ C/min, Fe = 0.5 mL/min, Fc = 0.02 mL/min (for 155–90  $^{\circ}$ C), and Fc = 0.01 mL/min (for 155–35  $^{\circ}$ C).

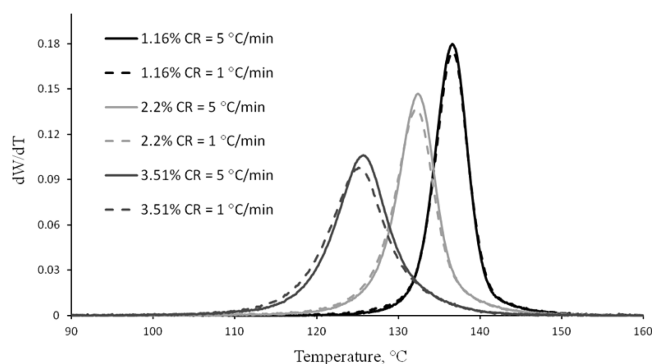


**Figure 4.** Effect of adsorption/desorption temperature range on HT-TGIC profiles for Blend-1. Experimental parameters: SZ = 400  $\mu$ L, CR = 5  $^{\circ}$ C/min, HR = 3  $^{\circ}$ C/min, Fe = 0.5 mL/min, Fc = 0.02 mL/min (155 – 90  $^{\circ}$ C), and Fc = 0.01 mL/min (155 – 35  $^{\circ}$ C).

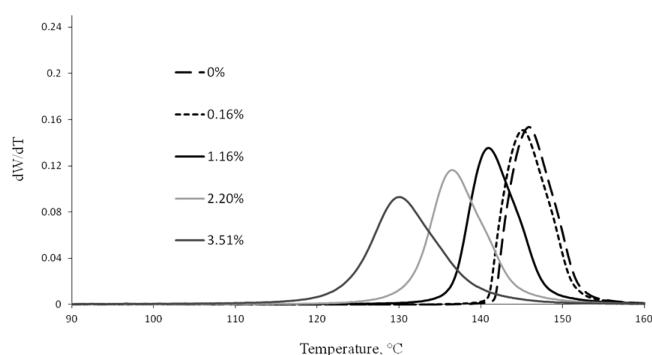
results obtained in the 155–35–160  $^{\circ}$ C and 155–90–160  $^{\circ}$ C ranges overlay almost completely, indicating that these resins were fully adsorbed at a temperature above 90  $^{\circ}$ C. Therefore, the HT-TGIC analysis of such resins can be done in a shorter time without affecting the quality of the obtained profile. These resins were also totally soluble in ODCB at 90  $^{\circ}$ C. Thus, HT-TGIC analyses in the 155–90–160  $^{\circ}$ C range were performed without formation of polymer crystals during the cooling cycle. Consequently, the fractionation can be considered to be free of cocrystallization effects that may reduce the resolution of crystallinity-based techniques such as TREF, CEF, and CRYSTAF.

**3.2. CR and HR Effects on HT-TGIC of Individual Resins.** Two cooling rates, 1 and 5  $^{\circ}$ C/min, were used to study their effect on the adsorption process. Figure 5 shows the chromatograms of samples m-2, m-4, and m-5 measured at these two cooling rates. The faster cooling rate leads to HT-TGIC profiles that are slightly narrower than those obtained at the slower cooling rate, but this effect does not seem to be very relevant in the cooling rate range investigated herein.

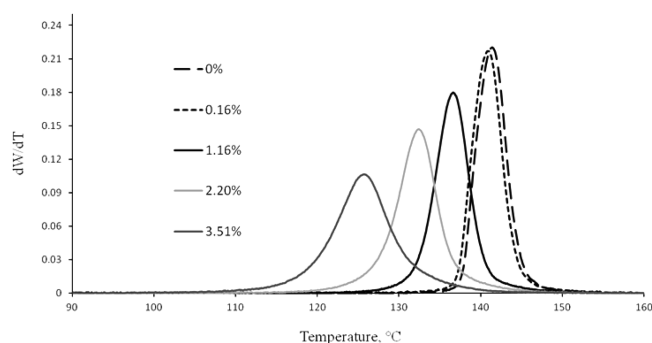
Figures 6 and 7 show the chromatograms of all individual resins (m-1 to m-5) using heating rates of 3 and 1  $^{\circ}$ C/min, respectively. The ethylene homopolymer elutes from the column at higher temperature and has a narrower profile than the ethylene/1-octene copolymers. As the comonomer content increases, the CCDs of ethylene/1-octene copolymers become broader and shift to lower temperatures. This behavior is theoretically expected and was also observed by Macko et



**Figure 5.** Effect of cooling rate on HT-TGIC profiles of individual resins. Experimental conditions: SZ = 400  $\mu$ L, HR = 3  $^{\circ}$ C/min, Fe = 0.5 mL/min, Fc = 0.02 mL/min (CR = 5  $^{\circ}$ C/min), and Fc = 0.01 mL/min (CR = 1  $^{\circ}$ C/min).

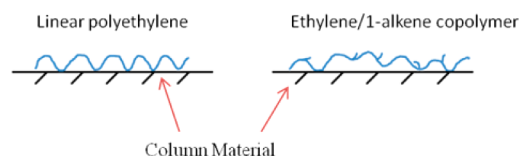


**Figure 6.** HT-TGIC profiles of individual resins. Experimental conditions: SZ = 400  $\mu$ L, CR = 5  $^{\circ}$ C/min (155–90  $^{\circ}$ C), Fc = 0.02 mL/min, HR = 3  $^{\circ}$ C/min, Fe = 0.5 mL/min.



**Figure 7.** HT-TGIC profiles of individual resins. Experimental conditions: SZ = 400  $\mu$ L, CR = 5  $^{\circ}$ C/min (155–90  $^{\circ}$ C), Fc = 0.02 mL/min, HR = 1  $^{\circ}$ C/min, Fe = 0.5 mL/min.

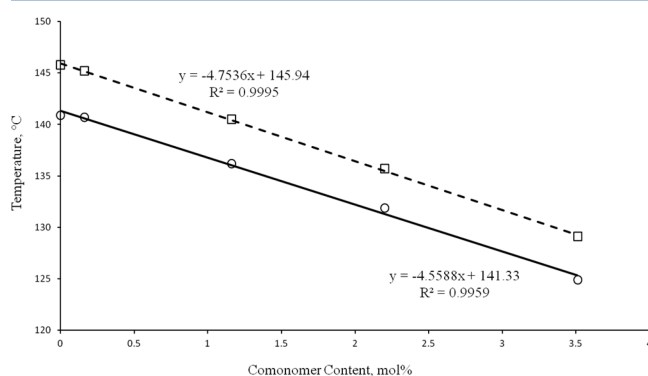
al.<sup>12</sup> for ethylene/1-hexene copolymers studied by HT-HPLC using a solvent gradient method. It can be attributed to a stronger adsorption of polyethylene chains without short chain branches onto the porous graphite surface, compared with that of ethylene/1-olefin copolymers. It has been suggested that polyethylene chains without short chain branches form closely packed monomolecular layers parallel to the graphite surface, as illustrated in Figure 8. The incorporation of  $\alpha$ -olefin molecules in the polymer chains form short chain branches that may sterically hinder the formation of these closely packed layers. Therefore, the presence of short chain branches disrupts chain adsorption and reduces their elution temperature. The analysis is very sensitive to comonomer content. The difference



**Figure 8.** Hypothetically, the presence of short chain branches hinders polymer chain adsorption on the graphite surface.

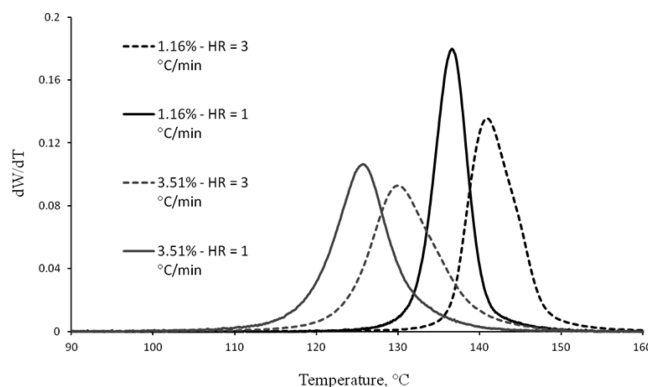
between an ethylene homopolymer and a copolymer with only 0.16 mol % of 1-octene is observed in Figures 6 and 7.

The relationship between elution peak temperature and comonomer content is approximately linear within this composition range and can be used as a calibration curve. From the resins studied in this work, two nearly parallel calibration curves were obtained for both heating rates, as shown in Figure 9.



**Figure 9.** Calibration curves for HT-TGIC using a heating rate of 3  $^{\circ}$ C/min (dashed line) and 1  $^{\circ}$ C/min (continuous line). Experimental conditions: SZ = 400  $\mu$ L, CR = 5  $^{\circ}$ C/min (155–90  $^{\circ}$ C), Fc = 0.02 mL/min, Fe = 0.5 mL/min.

The HT-TGIC profiles of all resins appear broader when measured at a heating rate of 3  $^{\circ}$ C/min, as shown in Figure 10.



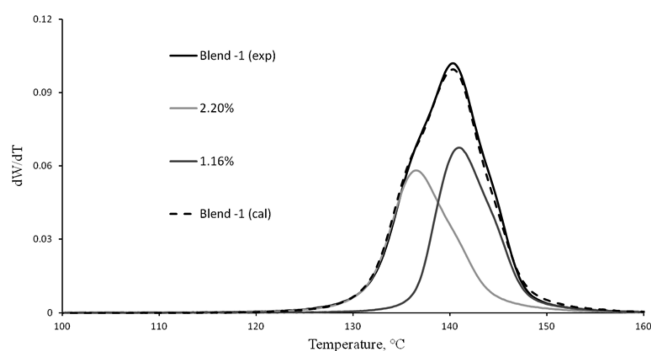
**Figure 10.** Effect of heating rate on the HT-TGIC profiles of individual resins. Experimental conditions: SZ = 400  $\mu$ L, CR = 5  $^{\circ}$ C/min (155–90  $^{\circ}$ C), Fc = 0.02 mL/min, Fe = 0.5 mL/min.

This increased broadness may be attributed to a more significant codesorption of the chains at the faster heating rate. A lower heating rate sharpens the HT-TGIC peaks and enhances peak resolution.

**3.3. HT-TGIC of Binary Blends.** The resolution of the HT-TGIC profiles was tested using the 50/50 wt % blends listed in Table 2. The experimental profile of Blend-1 as compared with



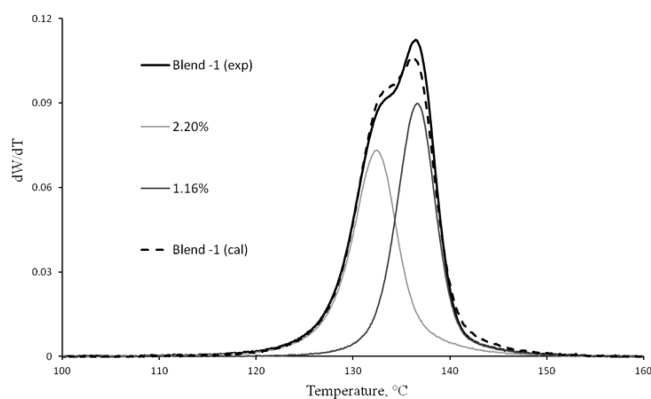
the chromatograms of the individual component resins is shown in Figure 11. The dotted line in Figure 11 represents the



**Figure 11.** HT-TGIC profile of blend-1 and its components. Experimental conditions: SZ = 400  $\mu$ L, CR = 5  $^{\circ}$ C/min (155–90  $^{\circ}$ C), Fc = 0.02 mL/min, HR = 3  $^{\circ}$ C/min, Fe = 0.5 mL/min.

profile of the blend calculated from the weighted sum of the experimental profile of each component obtained using the same run conditions. The components of blend-1, samples m-4 (2.2 mol % 1-octene) and m-3 (1.16 mol % 1-octene), have similar crystallizabilities. Adequate peak resolution between these components by crystallization-based techniques may be difficult to achieve due to significant cocrystallization effects. On the other hand, the experimental HT-TGIC profile using a cooling rate of 5  $^{\circ}$ C/min and a heating rate of 3  $^{\circ}$ C/min, matches the calculated one relatively well.

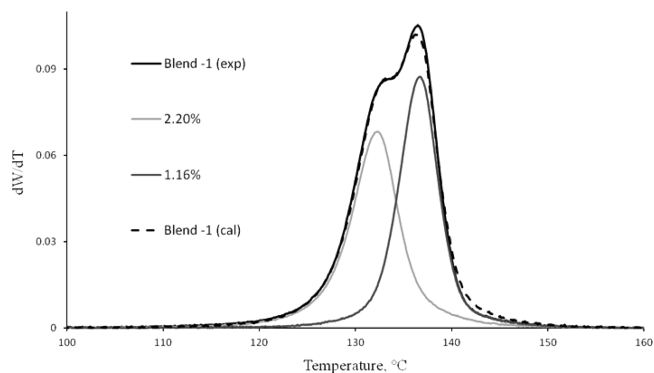
Peak separation for the components of blend-1 was improved by reducing the heating rate to 1  $^{\circ}$ C/min and keeping the cooling at 5  $^{\circ}$ C/min, as seen in Figure 12. Under these conditions, the experimental profile starts showing a shoulder at a temperature of approximately 134  $^{\circ}$ C.



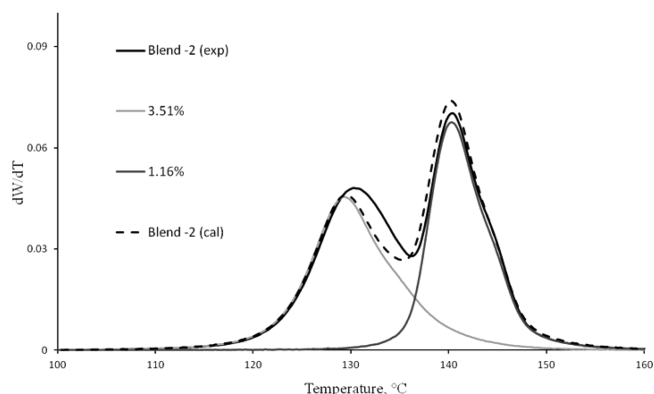
**Figure 12.** HT-TGIC profile of blend-1 and its components. Experimental conditions: SZ = 400  $\mu$ L, CR = 5  $^{\circ}$ C/min (155 – 90  $^{\circ}$ C), Fc = 0.02 mL/min, HR = 1  $^{\circ}$ C/min, Fe = 0.5 mL/min.

Figure 13 shows the HT-TGIC profile for blend-1 measured at a cooling and a heating rate of 1  $^{\circ}$ C/min. The best peak separation between the two blend components is achieved at these conditions, as well as excellent agreement between the calculated and experimental profiles for the blend.

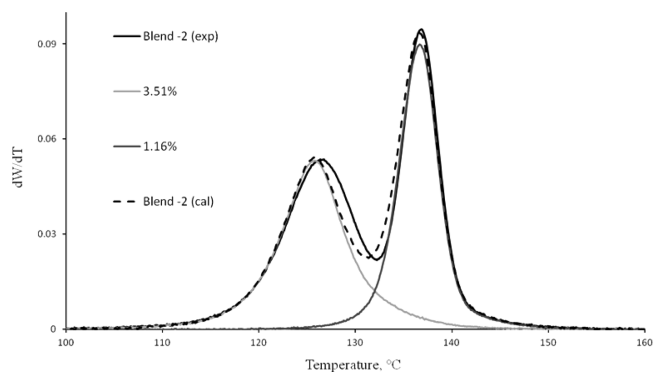
Blend-2, composed of samples m-5 (3.51 mol % 1-octene) and m-3 (1.16 mol % of 1-octene), was analyzed by HT-TGIC using heating rates of 3  $^{\circ}$ C/min and 1  $^{\circ}$ C/min. The results are shown in Figure 14 and 15, respectively. For both heating rates, the experimental profile of the blend did not match the



**Figure 13.** HT-TGIC profile of blend-1 and its components. Experimental conditions: SZ = 400  $\mu$ L, CR = 1  $^{\circ}$ C/min (155 – 90  $^{\circ}$ C), Fc = 0.02 mL/min, HR = 1  $^{\circ}$ C/min, Fe = 0.5 mL/min.



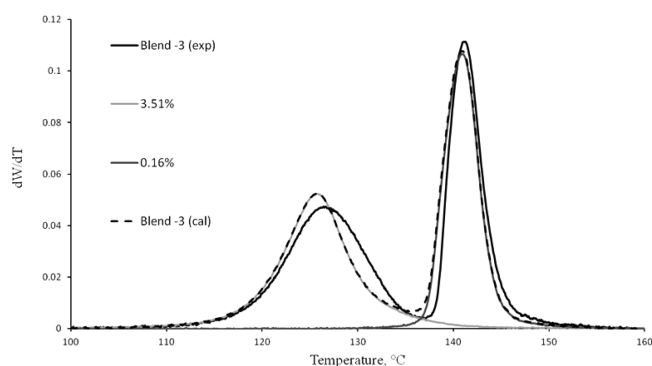
**Figure 14.** HT-TGIC profiles of blend-2 and its components. Experimental conditions: SZ = 400  $\mu$ L, CR = 5  $^{\circ}$ C/min (155 – 90  $^{\circ}$ C), Fc = 0.02 mL/min, HR = 3  $^{\circ}$ C/min, Fe = 0.5 mL/min.



**Figure 15.** HT-TGIC profiles of blend-2 and its components. Experimental conditions: SZ = 400  $\mu$ L, CR = 5  $^{\circ}$ C/min (155 – 90  $^{\circ}$ C), Fc = 0.02 mL/min, HR = 1  $^{\circ}$ C/min, Fe = 0.5 mL/min.

calculated one as well as for blend-1. Only a slight improvement was observed by reducing the heating rate to 1  $^{\circ}$ C/min; however, there is still a clear difference between the experimental and the predicted profile for blend-2, especially in valley between the two peaks.

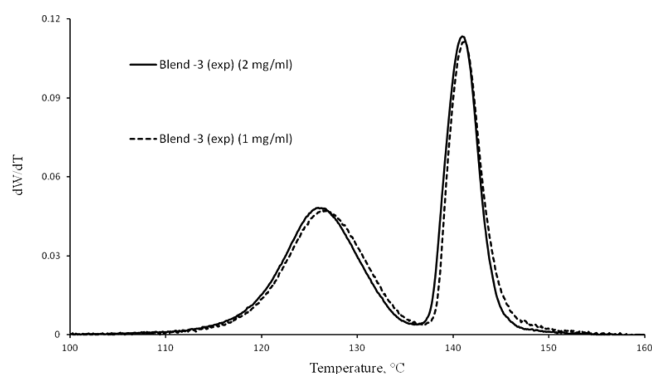
Similar differences were observed for Blend-3 in Figure 16. During the adsorption step, the component with 0.16 mol % 1-octene adsorbs at high temperature before the second component, since it has the lower comonomer content. It may be argued that the presence of these adsorbed chains on the graphite surface affects the adsorption of the second



**Figure 16.** HT-TGIC profiles of blend-3 and its components. Experimental conditions: SZ = 400  $\mu$ L, CR = 5  $^{\circ}$ C/min (155 – 90  $^{\circ}$ C), Fc = 0.02 mL/min, HR = 1  $^{\circ}$ C/min, Fe = 0.5 mL/min.

component. During the heating cycle, the component with high comonomer content in the blend elutes from the column at temperatures slightly higher than the elution temperatures of this component when analyzed individually. A similar argument may be proposed for blend-2. Blend-1 is apparently less affected by this effect, because its two components have very similar comonomer contents. The results shown for blend-2 and blend-3 seem to indicate that the peak separation for the blend components is affected by coadsorption and codesorption of polymer chains on the Hypercarb column.

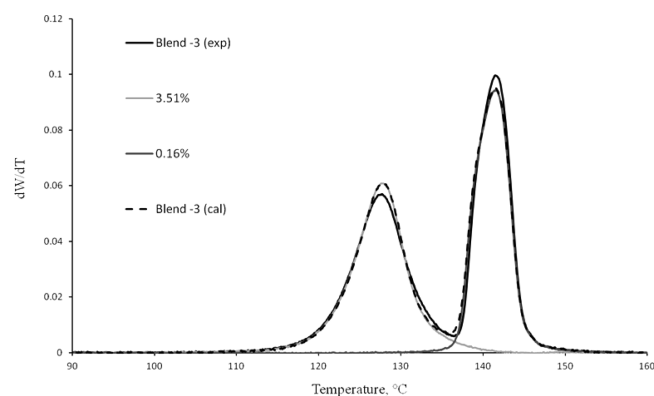
Trying to investigate this phenomenon in more depth, the sample concentration of blend-3 was reduced by 50% (from 2 to 1 mg/mL). However, no significant change was observed in the HT-TGIC curve, as illustrated in Figure 17, indicating that the observed phenomenon was not related to sample concentration.



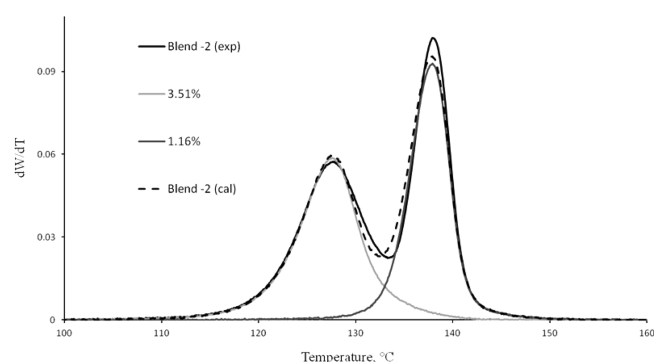
**Figure 17.** Effect of sample concentration on HT-TGIC profiles of blend-3. Experimental conditions: SZ = 400  $\mu$ L, CR = 5  $^{\circ}$ C/min (155–90  $^{\circ}$ C), Fc = 0.02 mL/min, HR = 1  $^{\circ}$ C/min, Fe = 0.5 mL/min.

Interestingly, reducing the volume of the sample injected into the column from 400 to 100  $\mu$ L, had a considerable influence on the results. The profile of blend-3 using a sample volume of 100  $\mu$ L is shown in Figure 18. At these conditions, a much better agreement between experimental and calculated profiles was observed. Similarly, the experimental profile for blend-2, depicted in Figure 19, improved considerably by reducing the sample volume to 100  $\mu$ L.

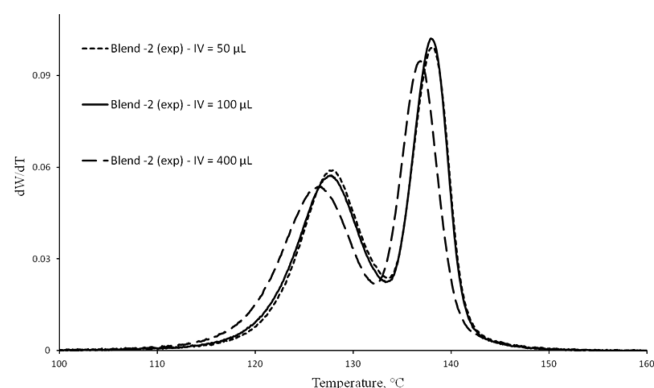
Figure 20 compares the profiles for blend-2 measured using injection volumes of 400, 100, and 50  $\mu$ L. Although a significant improvement was noticed when the sample volume decreased from 400 to 100  $\mu$ L, little change resulted when it was further



**Figure 18.** HT-TGIC profiles of blend-3 and its components. Experimental conditions: SZ = 100  $\mu$ L, CR = 5  $^{\circ}$ C/min (155–90  $^{\circ}$ C), Fc = 0.02 mL/min, HR = 1  $^{\circ}$ C/min, Fe = 0.5 mL/min.



**Figure 19.** HT-TGIC profiles of blend-2 and its components. Experimental conditions: SZ = 100  $\mu$ L, CR = 5  $^{\circ}$ C/min (155–90  $^{\circ}$ C), Fc = 0.02 mL/min, HR = 1  $^{\circ}$ C/min, Fe = 0.5 mL/min.



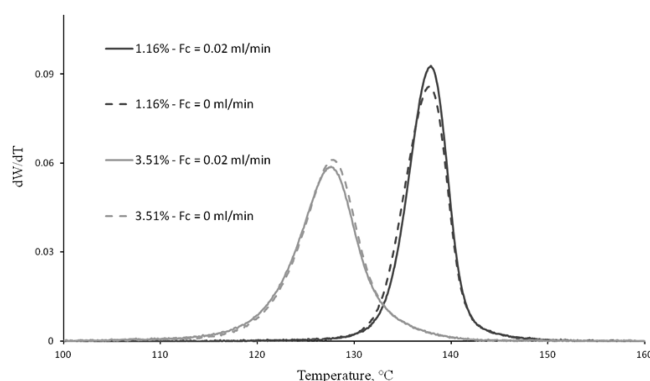
**Figure 20.** Effect of sample volume on HT-TGIC profiles for blend-2. Experimental parameters: CR = 5  $^{\circ}$ C/min (155–90  $^{\circ}$ C), Fc = 0.02 mL/min, HR = 1  $^{\circ}$ C/min, Fe = 0.5 mL/min.

decreased to 50  $\mu$ L. These results indicate that sample volume plays a major role in coadsorption and codesorption effects. It may be proposed that small sample volumes reduce the competition among the blend components adsorbing on the graphitic surface. In other words, column overloading decreases peak resolution of polyolefin blends in HT-TGIC analysis.

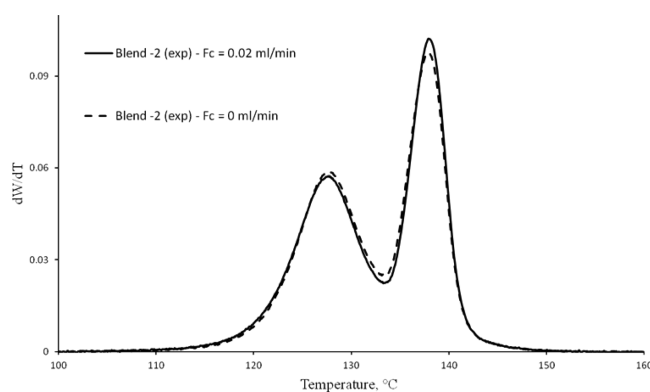
All the above-mentioned experiments were performed in “CEF mode”. A small amount of solvent was pumped through the column during the cooling cycle to allow for a more uniform deposition of polymer chains along the Hypercarb column. Blend-2 and its components were analyzed using

different solvent flow rates during the cooling step to further study the effect of the cooling flow rate ( $F_c$ ) on the resolution of the obtained profiles.

Interestingly, when the sample size was 100  $\mu\text{L}$  and the heating rate was 1  $^{\circ}\text{C}/\text{min}$ , the solvent flow rate during the cooling step had negligible effect on the HT-TGIC profiles. Figures 21 and 22 compare profiles measured with  $F_c = 0.02$  mL/min and 0 mL/min (TREF mode) for individual resins and blend-2, respectively.



**Figure 21.** Effect of solvent flow rate during the cooling step on HT-TGIC profiles of individual resins. Experimental conditions: SZ = 100  $\mu\text{L}$ , CR = 5  $^{\circ}\text{C}/\text{min}$  (155–90  $^{\circ}\text{C}$ ), HR = 1  $^{\circ}\text{C}/\text{min}$ , Fe = 0.5 mL/min.

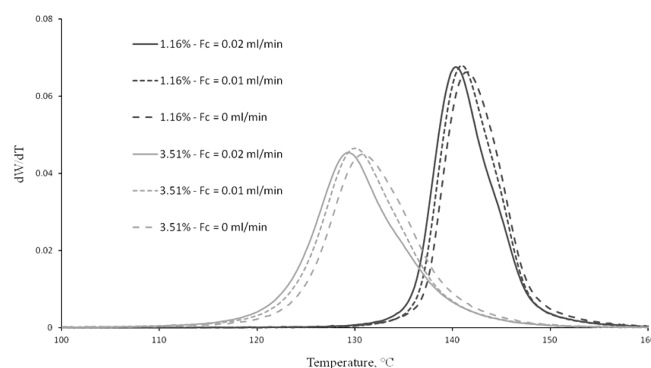


**Figure 22.** Effect of solvent flow rate during the cooling step on HT-TGIC profiles of Blend-2. Experimental conditions: SZ = 100  $\mu\text{L}$ , CR = 5  $^{\circ}\text{C}/\text{min}$  (155–90  $^{\circ}\text{C}$ ), HR = 1  $^{\circ}\text{C}/\text{min}$ , Fe = 0.5 mL/min.

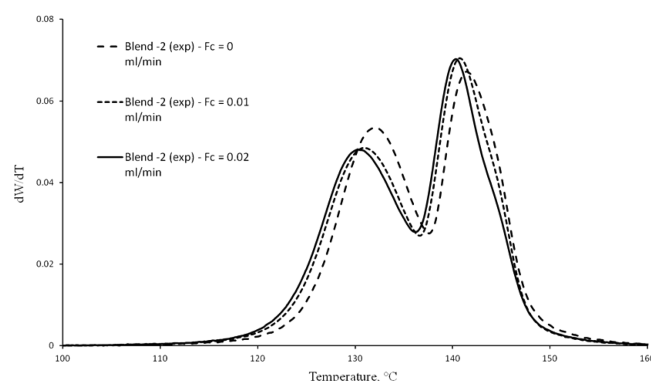
When using a heating rate of 3  $^{\circ}\text{C}/\text{min}$ , a small but significant flow rate effect was observed for blend-2 and its components when 400  $\mu\text{L}$  of each sample was injected into the column, as illustrated in Figures 23 and 24 for blend-2; the HT-TGIC profiles shifted to lower temperatures and became slightly sharper as  $F_c$  increased from 0 to 0.02 mL/min. A small increase in resolution seems to result from fractionating the polymer in CEF mode instead of in TREF mode for this set of conditions, likely because of the large sample volume of 400  $\mu\text{L}$  used in this case. Operation in CEF mode leads to a better distribution of the sample along the Hypercarb column, which may decrease the importance of coadsorption effects.

#### 4. CONCLUSIONS

The effect of operating conditions on HT-TGIC analysis have been studied using polyethylene and ethylene/1-octene copolymers made with a single-site catalyst. HT-TGIC fractionates polymer chains based on their interaction with



**Figure 23.** Effect of solvent flow rate during the cooling step on HT-TGIC profiles of individual resins. Experimental conditions: SZ = 400  $\mu\text{L}$  CR = 5  $^{\circ}\text{C}/\text{min}$  (155–90  $^{\circ}\text{C}$ ), HR = 3  $^{\circ}\text{C}/\text{min}$ , Fe = 0.5 mL/min.



**Figure 24.** Effect of solvent flow rate during the cooling step on HT-TGIC profiles of Blend-2. Experimental conditions: SZ = 400  $\mu\text{L}$  CR = 5  $^{\circ}\text{C}/\text{min}$  (155–90  $^{\circ}\text{C}$ ), HR = 3  $^{\circ}\text{C}/\text{min}$ , Fe = 0.5 mL/min.

porous graphitic carbon packing. The adsorption process takes place during the cooling cycle. The results indicate that this process is independent of the cooling rate within the range investigated in this study. Thus, to minimize analysis time, HT-TGIC runs can be performed using the fastest cooling rate and a narrow cooling cycle. The resins could also be analyzed at temperatures higher than their crystallization temperatures, thus avoiding cocrystallization effects.

The HT-TGIC elution peak temperatures depend linearly on the comonomer content. The obtained calibration curves at different heating rates are nearly parallel and shifted to high temperature as the heating rate increases.

The heating rate during desorption has a major effect on HT-TGIC profiles. Slower heating rates are required to enhance the resolution of individual resins and their blends. The chromatograms obtained with fast heating rate are broad and have low resolution, supposedly due to codesorption effects.

Sample volume is a very important parameter affecting the chromatograms of polyolefin blends. Experimental profiles for blends show good agreement with calculated ones when small sample volumes (equal to or less than 100  $\mu\text{L}$ ) are employed. This behavior may be attributed to stronger codesorption and/or codesorption effects when large sample volumes are injected to the column.

This systematic study shows that the HT-TGIC can be used to understand qualitatively the CCDs of individual resins and their blends with excellent resolution if the operating conditions are carefully optimized. Because so many variables can be manipulated during HT-TGIC analysis, a more in-depth



multivariate statistical analysis of this technique is currently under way in our group to deepen our understanding on how these different factors interact in HT-TGIC analyses.

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### Notes

The authors declare no competing financial interest.

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