



# Separating effective high density polyethylene segments from olefin block copolymers using high temperature liquid chromatography with a preloaded discrete adsorption promoting solvent barrier



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## ABSTRACT

Recent advances in catalyst technology have enabled the synthesis of olefin block copolymers (OBC). One type is a “hard-soft” OBC with a high density polyethylene (HDPE) block and a relatively low density polyethylene (VLDPE) block targeted as thermoplastic elastomers. Presently, one of the major challenges is to fractionate HDPE segments from the other components in an experimental OBC sample (block copolymers and VLDPE segments). Interactive high temperature liquid chromatography (HTLC) is ineffective for OBC separation as the HDPE segments and block copolymer chains experience nearly identical enthalpic interactions with the stationary phase and co-elute. In this work we have overcome this challenge by using liquid chromatography under the limiting conditions of desorption (LC LCD). A solvent plug (discrete barrier) is introduced in front of the sample which specifically promotes the adsorption of HDPE segments on the stationary phase (porous graphitic carbon). Under selected thermodynamic conditions, VLDPE segments and block copolymer chains crossed the barrier while HDPE segments followed the pore-included barrier solvent and thus enabled separation. The barrier solvent composition was optimized and the chemical composition of fractionated polymer chains was investigated as a function of barrier solvent strength using an online Fourier-transform infrared (FTIR) detector. Our study revealed that both the HDPE segments as well as asymmetric block copolymer chains (HDPE block length  $\gg$  VLDPE block length) are retained in the separation and the barrier strength can be tailored to retain a particular composition. At the optimum barrier solvent composition, this method can be applied to separate *effective* HDPE segments from the other components, which has been demonstrated using an experimental OBC sample.

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## 1. Introduction

Polyolefins are challenging to characterize due to their semi-crystalline nature, high melting temperature and resistance against many common solvents [1]. High temperature size exclusion chromatography (HT-SEC) is routinely practiced to determine polyolefin molecular weight (MW) and molecular weight distributions (MWD). However, determination of the chemical composition (CC) and distribution (CCD) is far more complicated [2] and often requires a multitude of chromatography and hyphenated (on-line

and/or off-line) techniques. Generally, crystallization based techniques such as analytical temperature rising elution fractionation (ATREF), crystallization elution fractionation (CEF), and crystallization analysis fractionation (CRYSTAF) are practiced to measure CC and CCD [3–7], but these methods are ineffective for amorphous materials. Further, different fractions of CCD often co-crystallize where polymer chains with different comonomer content interact during the crystallization process and upon re-dissolution co-elute. This affects the resolution of the separation and makes interpretation challenging especially for blends and polymers with a broad CCD. Recently, successful separation of polyolefin statistical copolymers has been realized through selective separation on porous graphitic carbon [8–11] using either solvent gradients [9,12–15] or thermal gradients [16–18]. The underlying mechanism of this sep-

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aration is *likely* preferential adsorption of ethylene sequences on graphitic carbon under selected thermodynamic conditions. Therefore, homopolymer polyethylene is strongly retained, while the introduction of *random* short chain branches of an alpha-olefin comonomer reduces retention and enables separating polyolefin statistical copolymers based on their comonomer content.

Recently olefin diblock copolymers (OBC) were developed as thermoplastic elastomers with targeted applications like foams and elastic films among others. In this work we studied an experimental “hard-soft” OBC. Both blocks of the OBC were ethylene-octene (EO) statistical copolymers with different ethylene to 1-octene ratios. The ethylene to 1-octene ratio is relatively high in the ethylene-rich “hard” block (high density polyethylene, HDPE block) compared to the “soft” block (relatively low density polyethylene, VLDPE block), and the blocks are polydisperse in molecular weight as well as in chemical composition. Characterization is further challenging as the sample contains block copolymer chains along with uncoupled HDPE and VLDPE chains. One of the existing challenges is to separate HDPE chains from the other components in the OBC sample (block copolymers and VLDPE chains) where crystallization-based techniques are not effective due to co-crystallization of the block copolymers and HDPE. On the other hand, the strength of interaction between the OBC and porous graphitic carbon surface has been found to correlate to the sum or total length of the HDPE [19]. Hence, this approach is also not efficient in separating HDPE chains from OBCs as they experience nearly identical enthalpic interactions with the stationary phase and co-elute (Supporting information, Section S1.0).

In this work, based on results originally published by Berek and coworkers [20–24], we report a novel adsorption-desorption based separation in the presence of a *discrete adsorption promoting solvent barrier* that can separate *effective* HDPE chains from the other components in the experimental OBC sample. We use the term *effective* to emphasize that the separated HDPE-rich fraction comprises both the HDPE monoblock chains and asymmetric block copolymer chains for which hard segment block length  $\gg$  soft segment block length. The separation has been successfully applied to an experimental OBC sample to fractionate *effective* HDPE chains from the other macromolecules present. Further, chemical compositions of the fractionated peaks were obtained across the elution profile using a composition sensitive detector. The strategy for optimum barrier solvent strength determination is discussed in detail along with the influence of barrier solvent composition on separation resolution. Finally, the efficacy and limitations of the discrete adsorption promoting solvent barrier based separation are considered.

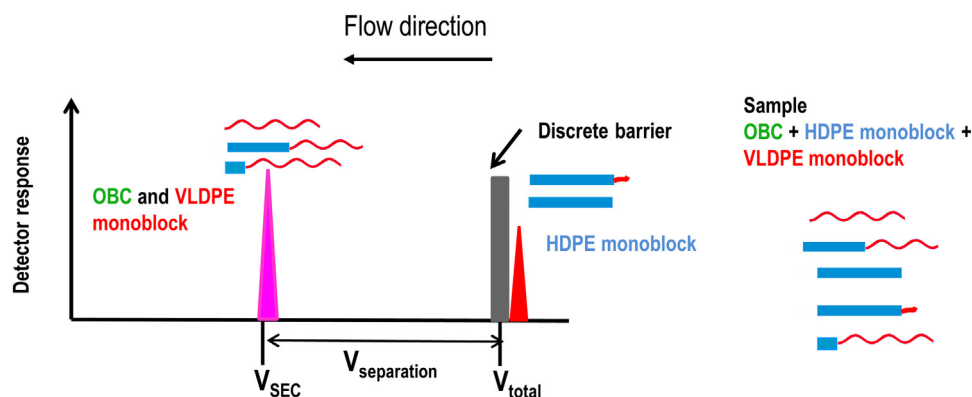
## 2. Discrete adsorption promoting solvent barrier method

The column interactions are broadly classified into two mechanisms: enthalpic and entropic. In size exclusion chromatography (SEC) mobile phase is selected to minimize enthalpic interaction and polymer chains are separated based on their hydrodynamic volume in the elution solvent. On the other hand, in interactive liquid chromatography enthalpic interaction between polymers and stationary phase dominates leading to separation sensitive to polymer chemical composition. However, in interactive liquid chromatography, entropic (SEC) contribution cannot be completely removed as porous packing materials are often used to increase the stationary phase surface area [25]. Between these two limits, a critical separation condition can be achieved where entropic and enthalpic contributions compensate each other. This is called liquid chromatography at the chromatographic critical condition (LC CC) where the molecular weight dependence of polymer species elution disappears. The LC CC is specifically useful for block copolymer

separation where one block can be eluted under critical condition and the other block elutes either in entropic (exclusion) or enthalpic (interaction) mode within a different retention volume. LC CC has been found to be successful in separating diblock from homopolymers when one of the parent homopolymers is *critically* eluted [26–28]. Recently, several sets of LC CC conditions were identified for linear polyethylene molecular weight standards and were used to separate statistical ethylene/1-octene copolymers of similar average molar mass [29]. While LC CC is an elegant separation process, this approach is highly sensitive to small changes in experimental conditions, especially the exact eluent composition [30]. Further, both theoretical and experimental studies report that both the chain length (equivalently MW) and CCD of the critically eluted block affect the retention of the other block [28,31,32]. This is specifically challenging for block copolymers where individual building blocks are copolymers with a chemical composition distribution. In this case the defined critical condition is true for only one specific copolymer composition and polymers on either side of this composition will either elute in exclusion (SEC) mode or enthalpic mode depending on which species is interacting with the column.

Discrete solvent barrier assisted separation, originally proposed by Berek and coworkers [20–23], utilizes a highly porous stationary phase (preferably with small pores) whose surface preferentially interacts with one of the blocks. While this is applicable to different interaction mechanisms (such as adsorption, precipitation, solubility, etc.) our study is focused on adsorption based separations only. It is anticipated that under similar thermodynamic conditions, the adsorption strength of the block copolymer containing one adsorbing block (HDPE segment) and one less/non-adsorbing block (VLDPE segment) would be lower than that of the adsorbing HDPE block alone (ethylene-rich monoblock). Thus a critical thermodynamic condition can be achieved using a discrete solvent plug (barrier) which will promote the adsorption of HDPE segments alone. Under these conditions, HDPE chains would adsorb on the column surface whereas other macromolecules would be able to cross the solvent plug. Further, the barrier permeable fraction (block copolymers and VLDPE monoblock chains) elutes ahead of the solvent plug in size exclusion mode. On the other hand, the retained fraction (HDPE monoblock chains) must follow the pore-included barrier solvent plug (through continuous adsorption-desorption sequences) and elute at the total volume of the column as a single molar mass-independent entity right after the barrier solvent plug elution. Since the polymer fraction that follows the barrier undergoes continuous adsorption-desorption sequences, this separation mechanism is referred to as *liquid chromatography under the limiting condition of desorption* (LC LCD) [23]. This idea is schematically presented in Fig. 1.

Now, we briefly discuss some experimental considerations necessary for HTLC in the presence of a discrete adsorption promoting solvent barrier. Porous graphitic carbon is a suitable candidate for a stationary phase (active surface) due to its known interactions with polyolefin. The mobile phase is expected to contain enough *desorli* (desorption promoting solvent or strong solvent) so that in the absence of any barrier (isocratic condition) the *strongest* adsorbing species (HDPE) would elute in the exclusion mode. This requirement confirms that there is no adsorption of *any* polymer species in the absence of a barrier and thus eliminates the possibility of any polymer chain precipitation and subsequently a mixed retention mechanism. For practical purposes, mobile phase solvent composition should be the minimum amount of *desorli* required to overcome interaction between the column and the most strongly adsorbing species (HDPE). In that case the mobile phase will act as a *desorli* for all the species and at the same time will minimize barrier solvent plug dilution through mixing during their transport along the column (chromatographic band broadening). The barrier solvent plug is tailored to promote adsorption of HDPE species in the



**Fig 1.** Schematic of the adsorption promoting discrete barrier solvent assisted separation profile as a function of retention volume. In actual experiment the barrier solvent plugs are invisible to the detector.

sample and allow elution of block copolymers and VLDPE species. To eliminate precipitation and minimize chromatographic band broadening, it is preferable to set the injection solvent composition identical to the mobile phase composition.

Finally, introduction of two different discrete solvent barriers are required to separate the materials into three compositionally distinct bins (block copolymer and two parent building blocks) in a *single* experiment. For a separation experiment with two discrete solvent barriers, determination of barrier strength/compositions, the relative positioning of barrier #1 with respect to barrier #2 and the sample, the mobile phase composition and flow rate considerations are *non-trivial* and can be found elsewhere [20,21]. Additionally, block copolymer composition, especially the number of blocks (di-, tri- etc.), overall content of the non-adsorbing block and the adsorbing block molar mass influence the barrier efficiency [33,34]. However, *effective* VLDPE chains (i.e. VLDPE monoblock and VLDPE-rich asymmetric diblock for which soft segment block length  $\gg$  hard segment block length) can easily be separated using conventional crystallization-based techniques as demonstrated in literature [35,36] or using interaction chromatography as shown in the present contribution (Supporting information, Section S1.0). Therefore, this study was devoted to develop a single discrete solvent barrier assisted separation of *effective* ethylene-rich monoblock chains from block copolymers and relatively low-ethylene content monoblock chains.

### 3. Materials and methods

#### 3.1. Polymer samples

The experimental polymer samples analyzed along with their unique identifiers used here are listed in Table 1. These samples were prepared using the synthesis scheme reported elsewhere [35]. The HDPE monoblock sample is expected to have the same composition and molecular weight distributions as the HDPE blocks in the OBC sample. The octene content in the HDPE block was  $\sim 0.2$  mol% (or 0.7%, w/w) as measured by  $^{13}\text{C}$  NMR. The measured OBC average/bulk octene content was  $\sim 3.4$  mol% (or, 12.5%, w/w).

**Table 1**

Description of the polymer samples analyzed in this study.

Sample designation	Description	Mw <sup>a</sup> (kg/mol)	PDI	Octene (C8) content <sup>b</sup> (mol%)	Octene (C8) content <sup>c</sup> (wt%)	Density (g/cc)
HDPE monoblock	EO statistical copolymer	99.2	1.90	$\sim 0.2$	$\sim 0.7$	0.958
OBC	Block copolymers with monoblocks	126.0	1.67	$\sim 3.4$	$\sim 12.5$	0.920

<sup>a</sup> From high temperature gel permeation chromatography (GPC).

<sup>b</sup> Measured by  $^{13}\text{C}$  NMR.

<sup>c</sup> Calculated from mol% data.

#### 3.2. High temperature liquid chromatography (HTLC)

HTLC experiments were conducted using a Polymer Labs PL-GPC-220 high temperature liquid chromatograph. Two graphitic Hypercarb<sup>TM</sup> columns (100 mm length, 4.6 mm i.d. and 250 Å pore size, Thermo Scientific) were used in series in this study. The exclusion and total volumes were measured [37] to be  $\sim 1.37$  and  $\sim 2.28$  mL, respectively, for both Hypercarb<sup>TM</sup> columns and connectors (between the columns and column to detector) combined. The column operating temperature was 170 °C. A Shimadzu LC-20AD pump was used to pump the mobile phase. 1,2-dichlorobenzene, ODCB (*desorli*) was used as mobile phase solvent. For all the experiments, the mobile phase flow rate was maintained at 0.5 mL/min. A combination of ODCB (*desorli*) and decane (*adsorli*) was used as the adsorption promoting discrete solvent barrier. All solvents (HPLC grade) were purchased from Fisher Scientific and used without any reagent addition or purification.

#### 3.3. Sample and discrete barrier solvent injection setup

Sample was injected using the PS-GPC-220 autosampler system. Samples were prepared at approximately 5 mg/ml in ODCB by shaking at 160 °C for 2 h. The vials were placed in the autosampler at 170 °C for  $\sim 1$  h prior to injection. A 10- $\mu\text{L}$  sample injection loop was used for all sample injections.

Barrier solvents for these experiments were introduced with an external Vici ABX0028 pneumatically operated 6-port valve. Prior to the start of each discrete barrier experiment approximately 500- $\mu\text{L}$  of the barrier was pushed through the 100- $\mu\text{L}$  injection loop while the external valve was in the load position. From previous experiments the volume in between the external (barrier) valve and the internal (sample) injection valves was found to be  $\sim 50$   $\mu\text{L}$  (Supporting information, Section S2.0).

Injection sequence was set up in such a way that there was a  $\sim 150$ - $\mu\text{L}$  volume gap between the barrier solvent and sample where the sample was injected after (behind) the barrier. This volume gap between the barrier plug and sample was necessary since if the barrier and samples were injected *almost* simultaneously then

any low-molar-mass or oligomeric admixture or impurity present in the sample would co-elute with the adsorbing macromolecules whose transport rate was hindered by the barrier solvent plug. In contrast, a large time delay between the sample injection and barrier would reduce the region of retention volumes available for separation. Typically a mobile phase flow rate of 0.5 mL/min. was used in these experiments. The volume gap was achieved by setting barrier and sample injection time at 4.67 and 4.97 min, respectively. Timing of the barrier injection was controlled using a Varian 850-MIB control box sending signal to the injection valve at the appropriate time. Note that the volume between the external and internal injection valves was  $\sim 50 \mu\text{L}$ . Hence, when sample was injected to the column, the discrete barrier solvent plug was expected to travel  $\sim 100 \mu\text{L}$  column volume.

### 3.4. Detectors

The detectors were an evaporative light scattering detector (ELSD) (Polymer Labs ELS1000) and an online full-spectrum infrared detector (DiscovIR-LC from Spectra Analysis, currently owned by Dani Instruments, Inc.). The ELSD detector allowed for simple detection of eluting polymer and was used for rapid method development. The ELSD operating parameters were: detector gas (nitrogen) flow rate of 1.4 L/min, nebulizer temperature of  $200^\circ\text{C}$  and evaporator temperature of  $270^\circ\text{C}$ .

The DiscovIR-LC was used to acquire full infrared spectra ( $650\text{--}4000 \text{ cm}^{-1}$ ) of non-volatile materials that eluted from the column at each retention time. A schematic of the instrument is shown in the Supporting information, Section S3.0. In the hyphen module, the LC eluent was thermally nebulized into an aerosol and rapidly desolvated. Next, the analyte stream was transferred to the DiscovIR with the help of a carrier gas (nitrogen) while the solvent was condensed and directed to waste. The analyte was deposited as a narrow track on a rotating, temperature-controlled ZnSe disk. Transmission infrared spectra were acquired as the track passed through the IR beam. Deposited tracks were rescanned at a slower rate to improve the signal/noise ratio. The following optimized DiscovIR conditions were used: nebulizer power: 10 W at 100% ODCB; cyclone temperature:  $305^\circ\text{C}$ ; condenser temperature:  $-5^\circ\text{C}$ ; carrier gas flow rate: 55 mL/min; disk temperature:  $50^\circ\text{C}$ ; acquisition parameters: 2 s/spectrum, 3 mm/min; and rescan parameters: 20 s/spectrum, 0.3 mm/min.

The octene content (% w/w) was calculated based on a calibration curve developed using a series of ethylene-octene (EO) statistical copolymers of known compositions. The octene content was calculated using the ratio of the  $\text{CH}_3$  bend peak area ( $\sim 1378 \text{ cm}^{-1}$ ) to the  $\text{CH}_2$  bend peak area ( $\sim 1465 \text{ cm}^{-1}$ ). The octene content is obtained by solving the following equation:

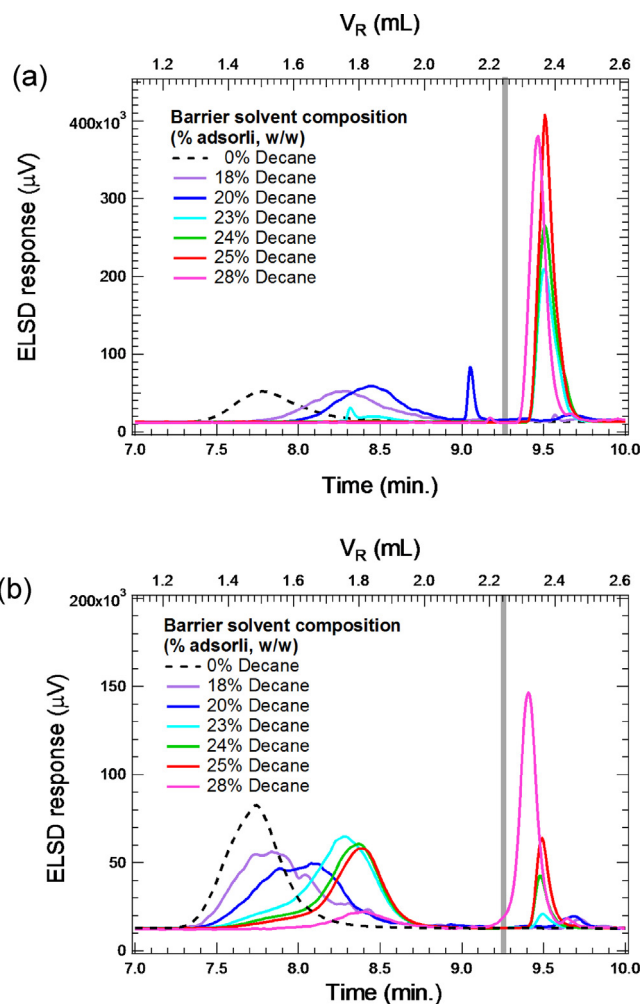
$$\frac{\text{CH}_3 \text{ peak area}}{\text{CH}_2 \text{ peak area}} = (-2.88E - 04)\alpha^2 + (3.45E - 02)\alpha + (2.33E - 01) \quad (1)$$

where  $\alpha$  is the octene content (% w/w). The details of chemical composition calibration using the DiscovIR detector are provided in the Supporting information, Section S3.0.

## 4. Results and discussions

### 4.1. Determination of optimum adsorption promoting solvent barrier composition

In terms of adsorption promoting strength for HDPE blocks, a barrier solvent can be classified as low, intermediate and high. If the barrier solvent adsorption promotion strength is low (i.e. low *adsorli* content), then all HDPE monoblock chains will be able to cross the barrier and elute in the size exclusion mode. If the barrier



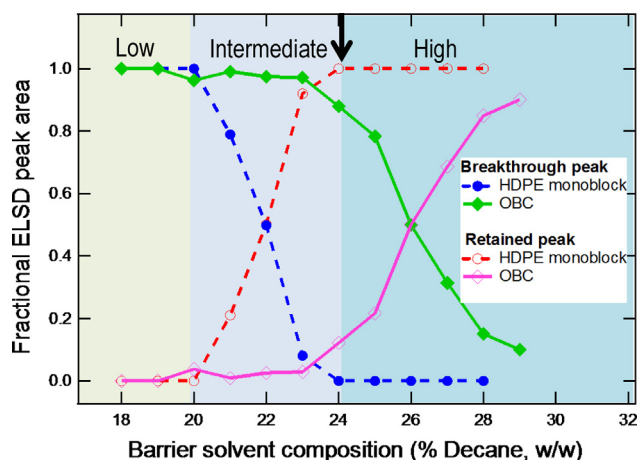
**Fig. 2.** Selected chromatograms (ELSD responses) of HTLC in the presence of a discrete adsorption promoting solvent barrier for (a) HDPE monoblock and (b) OBC samples for different barrier solvent compositions. All barrier composition values are presented in terms of adsorli content, % decane (w/w). The vertical bars represent estimated barrier solvent plug elution.

adsorption promotion strength is high, then no HDPE monoblock chains will be able to cross the barrier and all chains will elute after the barrier plug independent of their molar mass. For intermediate barrier adsorption promotion strength, a fraction of the HDPE monoblock chains will be able to cross the barrier while the other fraction will be retained giving rise to two peaks in detector response. For optimum barrier strength, the HDPE monoblock chains would just adsorb on the stationary phase (in the presence of the barrier) satisfying the limiting desorption condition.

To determine the optimum adsorption promoting discrete barrier solvent composition, a series of experiments were performed by introducing barriers of known compositions. Selected ELSD responses of the HDPE monoblock and OBC sample as a function of barrier strength are presented in Fig. 2a and b, respectively. Note that the barrier strength is presented as *adsorli* content (% w/w) in the barrier solvent plug. The barrier solvent plugs were invisible to the detector (local changes in eluent composition) and the barrier elution time assigned in Fig. 2(a) and (b) (vertical bars) are based on calculation (Supporting information, Section S2.0).

First a control experiment was performed under isocratic conditions in the absence of a barrier. In this case the sample was injected at 4.97 min without a preceding barrier injection. Under these conditions the polymer should elute in the size exclusion mode at  $\sim 2.74$  min. ( $V_{\text{SEC}} \sim 1.37 \text{ mL}$  and mobile phase flow rate





**Fig. 3.** Fractional peak areas determined from the area under ELSD peaks reported in Fig. 2(a) HDPE monoblock and (b) OBC samples under different barrier solvent compositions. Different barrier adsorption strength regimes, namely low, intermediate and high (from left to right) are shown here. The arrow marks the optimum barrier solvent composition.

0.5 mL/min.) after injection. Consistent with this expectation, the peak was observed at  $\sim 7.7$  min (dotted black trace, Fig. 2a and b) confirming polymer chain elution in the SEC region. For both samples (HDPE monoblock and the OBC) the peak was broad in nature due to the size exclusion effect.

At barrier solvent adsorpti content 18% w/w decane the HDPE monoblock peak was shifted to a later elution time (Fig. 2(a), purple trace) compared to the no barrier condition. It suggested the presence of some interaction between the column surface and HDPE monoblock chains. However, even at this barrier strength, all HDPE monoblock chains eluted in front of the barrier solvent plug (low barrier strength regime). Under the same barrier condition only a breakthrough peak was observed for the OBC (Fig. 2(b), purple trace) but much broader in nature and with distinct shoulders than that observed in the absence of a barrier. This was probably a convolution of the enthalpic (adsorption) and entropic (size exclusion) effect produced by a mixture of block copolymer chains and monoblock chains in the presence of a barrier solvent plug. Upon increasing the barrier strength to 20% w/w decane, two peaks appeared for the HDPE monoblock samples (Fig. 2(a), blue trace). Interestingly, both peaks appeared in front of the barrier plug. In this case, even when the barrier solvent composition belongs to low strength regime, some separation of chains was observed presumably arising from 1-octene content distributions. A further increase of barrier solvent strength to 23% w/w decane resulted in separation of the HDPE monoblock chains into two fractions (cyan trace). One negligibly small peak eluted in front of the barrier (breakthrough fraction) while most of the chains eluted after the barrier solvent plug elution (retained fraction). This suggests that barrier solvent composition is well within the intermediate strength regime and the transition from low to intermediate barrier strength occurred in between 20 and 23% (w/w) decane content for the HDPE monoblock sample (under these experimental conditions). A more precise low to intermediate barrier strength transition point was determined by running the separation in the presence of barriers with 21 and 22% (w/w) decane content (ELSD traces not shown) and is reported in Fig. 3 and related discussions. Finally, at close to or above a 24% (w/w) decane barrier solvent composition, (Fig. 2(a), green trace) the breakthrough peak vanished and almost all HDPE monoblock chains eluted after the barrier solvent plug elution confirming the intermediate to high barrier strength regime transition. Also note that the peak corresponding to the retained fraction (appeared at

$\sim 9.3$ – $9.6$  min) was relatively narrow in shape due to molar mass independent elution.

For the OBC sample (Fig. 2(b)), two peaks were observed in intermediate and strong barrier regimes suggesting fractionation of polymers where presumably the breakthrough fraction contained block copolymers and VLDPE monoblock chains and the retained fraction contained “effective” HDPE monoblock chains. At this point it should be acknowledged that block copolymers are generally heterogeneous in nature in terms of block length distribution. In a typical diblock system where individual building blocks are homopolymers, increasing molecular weight polydispersity in one or both blocks leads to increasing breadth of the block copolymer composition distribution. Even sequential anionic copolymerization of PS-*b*-PMMA was found to prepare a diblock having a distribution in block lengths [38]. In the case where one or both building blocks are random or statistical copolymers additional composition heterogeneity arises as building blocks contain both block length and chemical composition distribution. The experimental block copolymers studied here come from statistical copolymer building blocks having nearly Flory most probable molecular weight distributions. A 50:50 (by weight) diblock (AB) made from most probable molecular weight distribution building blocks (i.e.  $PDI_A = PDI_B = 2.0$ ,  $PDI_k = (M_w/M_n)$ ) produces a statistical distribution of diblock compositions resulting in an equal weight fraction of diblock copolymer chains at every possible block fraction [39]. Therefore, we expect the presence of some highly asymmetrical block copolymer chains in our experimental samples. An asymmetric block copolymer chain with very short non-interacting polymer segment (i.e. soft segment block length  $\ll$  hard segment block length) may also be retained by the barrier and elute after it. Considering this possibility, we hypothesized that the retained fraction of the OBC sample consisted of HDPE monoblock and some asymmetric block copolymer chains with HDPE block length  $\gg$  VLDPE block length.

The low, intermediate and high barrier strengths can be expressed quantitatively in terms of fractional peak area values defined as:

$$\text{fractional peak area} = \frac{\text{Area under a specific peak}}{\text{Area under all peaks observed in ELSD response.}} \quad (2)$$

We label the peak eluting in front of the barrier solvent plug as the *breakthrough peak* and the one eluting after as the *retained peak*. It should be recognized that ELSD responses are non-linear in terms of polymer concentration and have been reported to exhibit analyte chemical composition bias [14,40,41]. However, in this case, for a given sample a fixed polymer concentration was used for experiments conducted under different barrier solvent strengths. Therefore, detector response artifact in fractional peak area calculation was expected to be small (originating from peak shapes). Based on our designation of barrier solvent strength (low, intermediate and high), the fractional peak areas for HDPE monoblock chains are expected to be: (a) a fractional breakthrough peak area 1.0 and a fractional retained peak area 0.0 at low barrier strength regime; (b) both the fractional breakthrough and retained peak areas in between 0.0 and 1.0 at intermediate barrier strength regime; and (c) a fractional breakthrough peak area is 0.0 and a fractional retained peak area is 1.0 at high barrier strength regime. For the OBC at low barrier strength regime, the fractional breakthrough peak area should be 1.0. In the intermediate and high barrier strength regimes both the breakthrough and retained fractional peak areas should be between 0.0 and 1.0 due to the presence of VLDPE and VLDPE-rich asymmetric diblocks in the OBC sample.

Based on the ELSD traces presented in Fig. 2(a) and (b), fractional (breakthrough and retained) peak areas were calculated and

are presented in Fig. 3. At low decane content in the barrier solvent, for both the HDPE monoblock and OBC samples, the fractional breakthrough peak areas were 1.0. With increasing *adsorli* (decane) content in the barrier solvent, the fractional breakthrough peak area started to decrease with a concomitant increase in fractional retained peak area. The transition from low to intermediate regime occurred at a barrier solvent composition between 20 and 21% (w/w) decane content for the HDPE monoblock chains. For the OBC sample the same transition occurred at a higher barrier *adsorli* (decane) content.

It is hypothesized that the slope of the sigmoidal curve in the intermediate barrier strength region is primarily associated with the breadth of the chemical composition distribution of the sample, but molecular weight and its distribution are also likely to contribute. For the HDPE monoblock, the chemical composition distribution arises from comonomer content of the chains. In the absence of a composition distribution and with a narrow molecular weight distributions, all chains should exhibit the same interaction (adsorption) strength with the column surface and at a specific barrier solvent strength all chains would adsorb on the column surface. Under those *ideal* conditions, instead of sigmoidal curves, the breakthrough and retained fractional peak areas in Fig. 3 would be step functions. This was indeed observed when adsorptions promoting discrete barrier experiments were performed for a polyethylene (PE) homopolymer standard (data not shown). But in reality, a chemical composition distribution is always present in a copolymer and should be reflected in the width of the sigmoidal transitions. The chemical composition distribution of the OBC sample had one additional degree of chemical compositional heterogeneity arising from block length distributions. A larger barrier solvent transition width for the OBC was expected and indeed observed (Fig. 3). Based on Fig. 3, the *optimum* barrier composition is defined as the condition at which intermediate to strong barrier regime transition occurs for the HDPE monoblock (marked by black arrow in Fig. 3). At that condition barrier solvent plug would retain all *effective* HDPE chains and allow the block copolymers and VLDPE monoblock chains pass through. Chromatograms obtained for the HDPE monoblock and OBC samples under optimum barrier conditions are presented in Fig. 4.

#### 4.2. Chemical compositions of the breakthrough and retained fractions

In the presence of the optimum adsorption promoting barrier solvent plug defined in the previous section, all HDPE monoblock chains and some HDPE-rich asymmetric block copolymer chains were retained by the barrier. When the barrier solvent adsorption strength is lower than the optimum condition (i.e. with a lower *adsorli* content), some HDPE monoblock chains eluted with the breakthrough fraction. In contrast, for the barrier solvent composition with higher *adsorli* content than optimum, some additional block copolymer chains (besides only the highly asymmetric ones) were retained along with HDPE monoblock chains. Therefore, it is important to understand the chemical compositions of the break-

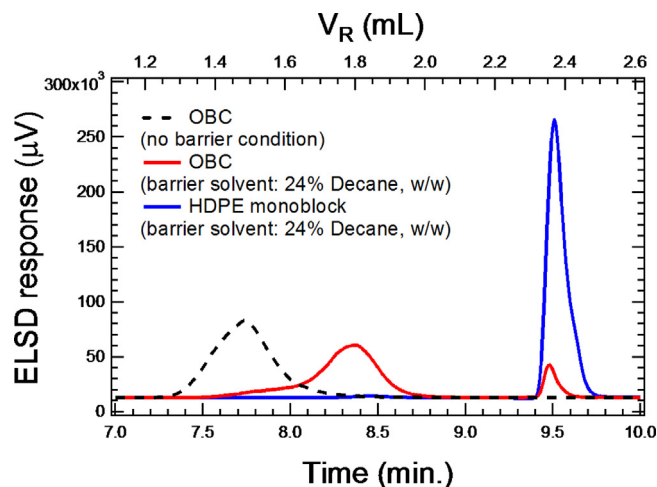


Fig. 4. Separation of the OBC from effective HDPE monoblock chains in the presence of optimum barrier solvent compositions. For reference, ELSD traces collected for the OBC in the absence of barrier is also shown.

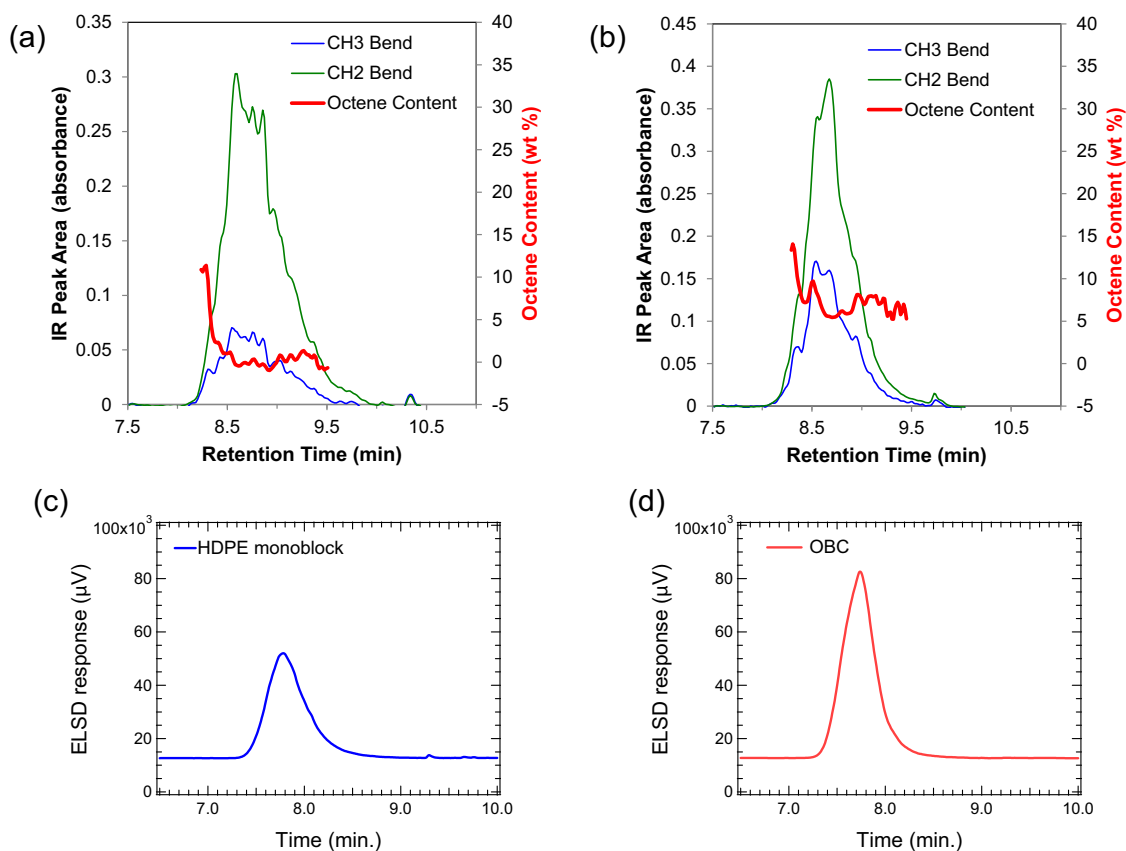
through and retained fractions at and close to the optimum barrier solvent compositions. For this purpose, an FTIR detector was used to characterize the chemical compositions of the breakthrough and retained peaks.

FTIR and ELSD chromatograms of the control experiments (no barrier) are shown in Fig. 5(a)–(d). The FTIR chromatograms are similar to the ELSD chromatograms but somewhat broader due to the sample desolvation/deposition process and the linear response of the DiscovIR. The apparent difference in retention time between the FTIR and ELSD chromatograms ( $\approx 1$  min) was due to the lag between when the sample was deposited on the ZnSe disk and when the FTIR spectrum was acquired in the DiscovIR instrument. The octene content of the HDPE monoblock sample decreased sharply at the leading edge of the peak and maintained a plateau thereafter. Similar observation was noted for the octene content of the OBC sample peak. It suggested that within a single peak low-octene content VLDPE monoblock chains eluted first, followed by the block copolymer and then the HDPE monoblock chains based on their architecture and ethylene content. Also there appears to be higher octene at higher  $M_w$  for the HDPE monoblock sample (Fig. 5(a)) – this could be real, but could also be due to low signal/noise at the extremes of the peak. Adsorption of HDPE monoblock chains on graphitic carbon using ODCB as mobile phase at 170 °C would not be expected. From the FTIR data, the average octene contents were found to be  $\sim 0.4\%$  and  $7.1\%$  (w/w) for the HDPE monoblock and OBC samples, respectively. For both samples the octene content obtained from FTIR was slightly lower compared to the  $^{13}\text{C}$  NMR-measured value. Considering the difference in measurement techniques and associated uncertainties, in general, the FTIR and NMR-measured octene contents are in agreement as reported in Table 2.

Table 2  
Comparison of octene (C8) content measured using  $^{13}\text{C}$  NMR and HTLC-FTIR techniques.

Sample	C8 from $^{13}\text{C}$ NMR (% w/w)	C8 from FTIR (% w/w)			
		No barrier condition	Optimum barrier condition (24% Decane, w/w)		
			Overall <sup>a</sup>	Breakthrough fraction	Retained fraction
HDPE monoblock	$\sim 0.7$	0.4	0.5	18.4	0.2
OBC	$\sim 12.5$	7.1	8.8	11.1	3.3

<sup>a</sup> Weighted average (by FTIR peak areas) of both the breakthrough and retained fractions.



**Fig. 5.** Top: LC-FTIR chromatograms of the (a) HDPE monoblock and (b) OBC samples collected in the absence of any adsorption promoting solvent barrier. Bottom: ELSD chromatograms of the (c) HDPE monoblock and (d) OBC samples collected in the absence of any adsorption promoting solvent barrier.

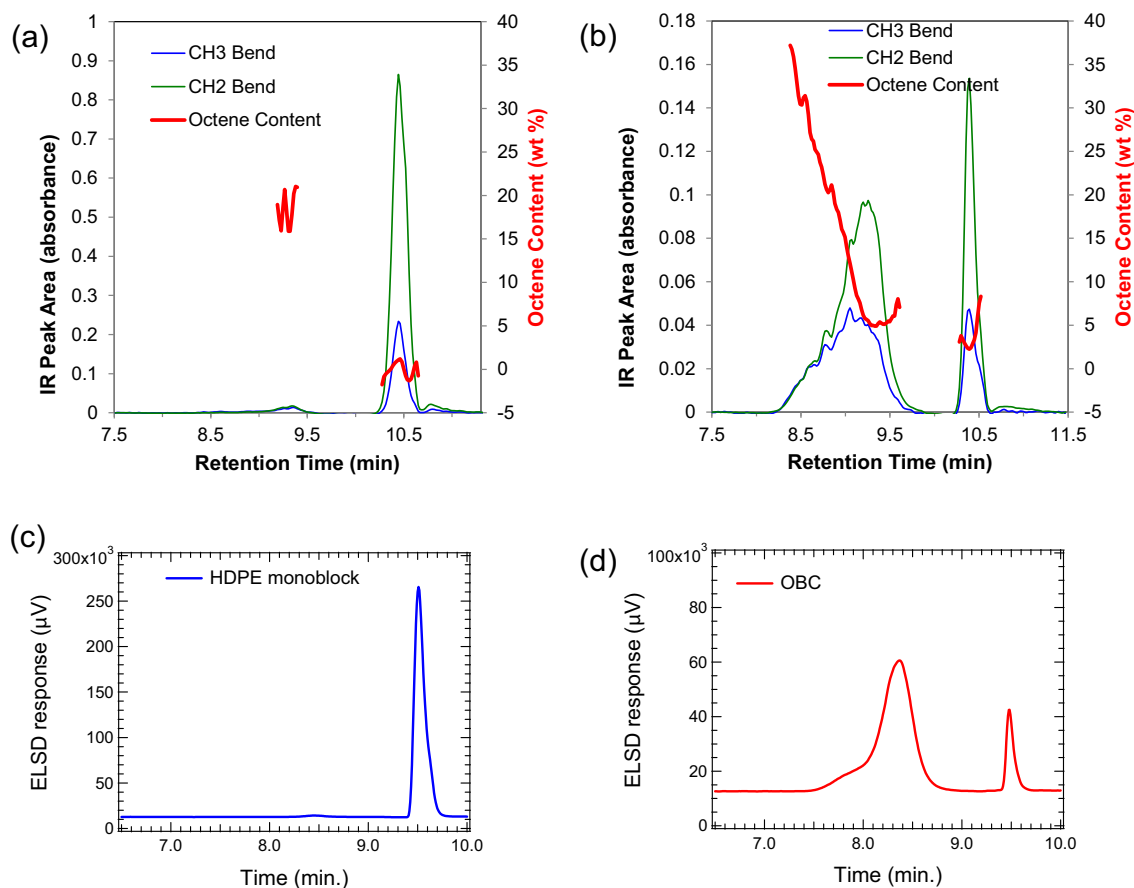
FTIR chromatograms collected in the presence of optimum barrier solvent plug, 24% w/w decane, are shown in Fig. 6. A negligibly small breakthrough fraction was observed with extremely high (~18%, w/w) octene content. The average octene content of the retained peak by FTIR was ~0.2% w/w. The overall octene content was ~0.5% (w/w) which was close to the NMR-measured value of ~0.7% w/w (Table 2). Note that under the same experimental conditions a homopolymer high density polyethylene standard eluted as a single retained peak whereas, an EO statistical copolymer with 2.6 mol% octene content (9.65 wt% octene) eluted as a single breakthrough peak (Supporting information, Section S4.0).

In contrast to the HDPE monoblock, the OBC sample exhibited a broad octene distribution. The leading edge of the breakthrough peak contained ~37% (w/w) octene, much higher than NMR-measured OBC average octene content ~12.5% (w/w). This population mainly consists of VLDPE monoblock chains and VLDPE-rich asymmetric diblock chains. The octene content then gradually decreased to ~5% w/w, and finally increased at the trailing edge of the breakthrough peak. The average octene content of the breakthrough fraction was 11.1% (w/w). The decrease in octene content from ~37% (w/w) to ~5% (w/w) was due to the broad composition distribution of the block copolymer. The greater the weight fraction of octene in the VLDPE block, the sooner it breaks through the barrier, and hence, the earlier the elution. The increase in octene content at the trailing edge of the breakthrough peak was attributed to a combination of adsorption and size exclusion effects. ODCB is a reasonably strong solvent, but the large pores (average size 250 Å) of the Hypercarb™ column separate the chains by molecular weight. Some low molecular weight VLDPE monoblock and low molecular weight asymmetric diblock chains were responsible

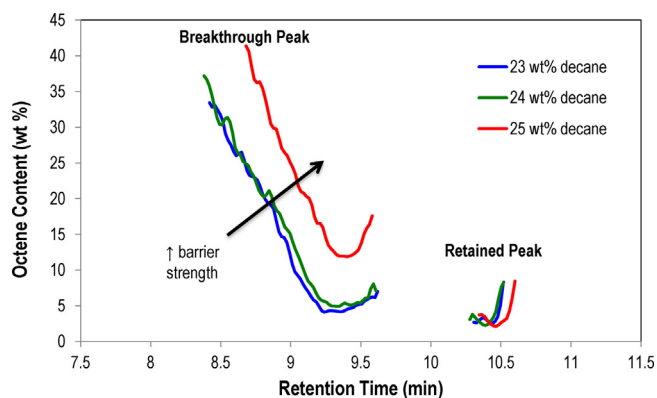
for the apparent increase in octene content at trailing edge (~FTIR retention time of ~9.5 min, Fig. 6b). This size exclusion effect was verified using PE homopolymer molecular weight standards under isocratic conditions using ODCB as mobile phase solvent (Supporting information, Section S5.0).

The octene content of the retained peak started at the same octene content as the minimum of the breakthrough peak. It decreased rapidly to ~2% (w/w) octene and then increased. The average octene content of the retained peak was ~3.3% (w/w), which was substantially higher than the measured average octene content of the HDPE block (~0.7%, w/w). This higher average octene content can only be explained by the presence of some block copolymer chains (presumably asymmetric) in the retained fraction that had similar adsorption properties as the HDPE monoblock. On average, the retained block copolymer chains must have higher octene content than the HDPE monoblock and as a result, the average octene content of the retained peak was higher than the average/bulk value.

This general trend in the OBC breakthrough and retained peak chemical composition distributions was observed for all selected barrier solvent compositions that were investigated (Fig. 7). FTIR chromatograms obtained on the OBC samples used to prepare Fig. 7 are presented in Supporting information, Section S6.0. In all cases the breakthrough peak leading edge octene content started from ~33–41% (w/w) and gradually decreased to a minimum. The negative slope in octene content was hypothesized to be due to the composition distribution. In this case the same OBC sample was fractionated using solvent barrier plugs of different adsorption promoting strength and hence, the slope was found largely unchanged. In contrast, the minimum value of octene content



**Fig. 6.** Top: FTIR chromatograms of the (a) HDPE monoblock and (b) OBC samples at optimum barrier condition (24% decane, w/w). Bottom: ELSD chromatograms of the (c) HDPE monoblock and (d) OBC samples at optimum barrier condition (24% decane, w/w).



**Fig. 7.** Octene content distributions of the OBC for different barrier solvent compositions.

was found to be increasing with increasing adsorption promoting strength of the barrier solvent. This suggested higher cut-off in terms of overall block copolymer octene content as the *adsorli* content in the barrier solvent plug increased. Finally, at the trailing edge of the breakthrough peak the octene content increased for all barrier solvent compositions studied here. This increase in octene content primarily arose from the size-exclusion effect (low molecular weight relatively low-ethylene content chains) and was expected to be unaffected by any variations in barrier solvent strength.

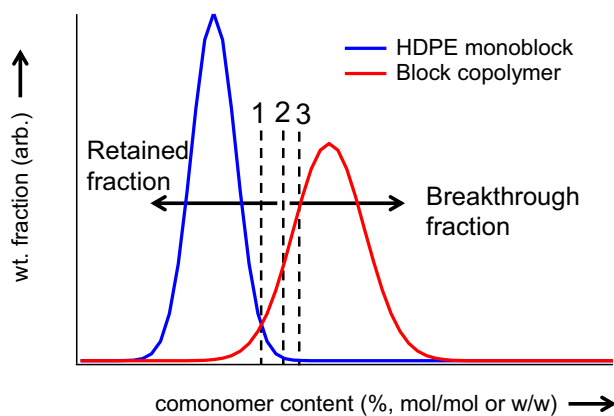
The retained peak followed a similar composition trend with barrier strength as the breakthrough peak. The octene content of

the retained peak started at the same value irrespective of the barrier *adsorli* content. It decreased at first followed by an increase with a slope independent of the barrier adsorption promoting strength.

#### 4.3. Interpretation of the adsorption promoting discrete barrier experiment

These experiments demonstrate that the adsorption barrier separation retains polymer chains as a function of block ratio, comonomer content and random/statistical vs. block architecture. Polymer chains with high ethylene content (HDPE-rich asymmetric block copolymers and HDPE monoblock) are retained in the separation, and the barrier strength can be tailored to retain a particular composition as well as all chains with higher HDPE block content. Also, due to finite porosity of the Hypercarb™ column the breakthrough and retained peaks are impacted by both chemical composition and molecular weight distributions. A schematic of these conclusions is shown in Fig. 8. If the HDPE monoblock and block copolymer chains composition distributions (overall comonomer content) are well separated without any overlap in area then fractionation at optimized barrier solvent strength condition would provide the exact and true separation of HDPE monoblock chains. But as long there is any overlap, as shown in Fig. 8, determination of the free HDPE segment in the OBC product using a barrier method will always be subjected to the selection of barrier strength. As the barrier solvent adsorption promoting strength increases, block copolymer chains with a higher overall comonomer content are retained by the barrier solvent plug, because a larger fraction of the block copolymer chains effectively





**Fig. 8.** Schematic for interpreting adsorption barrier experiments. In terms of barrier solvent adsorption promoting strength: Barrier 1 < Barrier 2 < Barrier 3. Dotted vertical lines represent the chemical composition that is effectively retained by the barrier solvent plug in a given experimental condition. Note that the HDPE monoblock used in this study was an ethylene-octene (EO) statistical copolymer with an extremely high ethylene to 1-octene ratio.

behave as HDPE monoblock chains in terms of their adsorption on the porous graphitic surface.

## 5. Summary

One of the existing challenges in polyolefin characterization is to separate any HDPE monoblock chains present in OBC samples. HDPE monoblock chains and block copolymers co-elute when traditional interaction chromatography techniques are applied. In this study we have demonstrated separation of HDPE monoblock chains using a discrete adsorption promoting solvent barrier. The composition of the barrier solvent was optimized to promote adsorption of HDPE monoblock chains using a sample containing only HDPE monoblock and representative of the hard segment of the experimental OBC sample. When the optimized barrier condition was applied to experimental OBC samples, HDPE-rich asymmetric block copolymer chains were also retained. In contrast, block copolymers and VLDPE monoblock chains could cross the barrier solvent plug and being pore-excluded eventually got separated from the *effective* HDPE monoblock chains. Further, the efficacy and limitations of the adsorption promoting barrier based separation method have been evaluated by monitoring the breakthrough and retained peak chemical compositions as a function of barrier solvent adsorption promoting strength.

Our results show that selective adsorptions of polymer chains are very sensitive to experimental conditions particularly to barrier solvent strength and the composition distribution of the HDPE monoblock. Polymer chains with high comonomer content (block copolymers and VLDPE monoblock) break through the barrier. In contrast, polymer chains with high ethylene content (HDPE-rich asymmetric block copolymers and HDPE monoblock) are retained. The breakthrough and retained peaks are impacted by both chemical composition and molecular weight distributions. The separation cut-off of comonomer content depends on barrier strength and can be tailored to retain a particular composition and all chains having higher HDPE monoblock content. Finally, the barrier method is most effective at separating pure monoblock when there is no or negligible overlap between the chemical composition distribution curve of the HDPE monoblock and block copolymer chains. However, we caution that even at that condition, from an adsorption point of view, an extremely asymmetric HDPE-rich asymmetric block copolymer chain would behave like HDPE monoblock chain. On the other hand, in case of overlap in chemical composition distribution, the separation comonomer content cut-off will depend

on barrier strength. At optimum adsorption promoting barrier solvent composition, this method can be applied to separate *effective* HDPE monoblock chains contained within these experimental OBC samples.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chroma.2016.08.055>.

## References

- [1] T. Macko, R. Brüll, Y.T. Zhu, Y. Wang, A review on the development of liquid chromatography systems for polyolefins, *J. Sep. Sci.* 33 (2010) 3446–3454.
- [2] S. Anantawaraskul, Chemical Composition Distribution of Binary and Multicomponent Copolymers in Ph. D Thesis, Department of Chemical Engineering, McGill University, Montreal, 2003.
- [3] S. Anantawaraskul, J.B.P. Soares, P.M. Wood-Adams, Fractionation of semicrystalline polymers by crystallization analysis fractionation and temperature rising elution fractionation, *Polym. Anal. Polym. Theory* 182 (2005) 1–54.
- [4] B. Monrabal, Crystallization analysis fractionation – a new technique for the analysis of branching distribution in polyolefins, *J. Appl. Polym. Sci.* 52 (1994) 491–499.
- [5] B. Monrabal, N. Mayo, L. Romero, J. Sancho-Tello, Crystallization elution fractionation: a new approach to measure the chemical composition distribution in polyolefins, *Lc Gc Eur.* (2011) 18–19.
- [6] J.B.P. Soares, S. Anantawaraskul, Crystallization analysis fractionation, *J. Polym. Sci. Part B Polym. Phys.* 43 (2005) 1557–1570.
- [7] L. Wild, Temperature rising elution fractionation, *Adv. Polym. Sci.* 98 (1991) 1–47.
- [8] T. Macko, H. Pasch, Separation of linear polyethylene from isotactic, atactic, and syndiotactic polypropylene by high-temperature adsorption liquid chromatography, *Macromolecules* 42 (2009) 6063–6067.
- [9] M.D. Miller, A.W. deGroot, J.W. Lyons, F.A. Van Damme, W.L. Winniford, Separation of polyolefins based on comonomer content using high-temperature gradient adsorption liquid chromatography with a graphitic carbon column, *J. Appl. Polym. Sci.* 123 (2012) 1238–1244.
- [10] F.A. Van Damme, J.W. Lyons, W.L. Winniford, A.W. deGroot, M.D. Miller, Chromatography of Polyolefin Polymers, in: U.S. Patent (Ed.), US 8,476,076 B2, Dow Global Technologies LLC, 2013.
- [11] W.L. Winniford, R. Cong, T.M. Stokich, R.J. Pell, M.D. Miller, A. Roy, F.A. Van Damme, A.W. deGroot, J.W. Lyons, D.M. Meunier, Chromatography of Polyolefin Polymers, in: U.S. Patent (Ed.), US 8,318,896 B2, Dow Global Technologies LLC, 2012.
- [12] R. Chitta, A. Ginzburg, G. van Doremaele, T. Macko, R. Brüll, Separating ethylene-propylene-diene terpolymers according to the content of diene by HT-HPLC and HT 2D-LC, *Polymer* 52 (2011) 5953–5960.
- [13] T. Macko, R. Brüll, R.G. Alamo, Y. Thomann, V. Grumel, Separation of propene/1-alkene and ethylene/1-alkene copolymers by high-temperature adsorption liquid chromatography, *Polymer* 50 (2009) 5443–5448.
- [14] T. Macko, R. Brüll, Y. Wang, B. Coto, I. Suarez, Characterization of ethylene-propylene copolymers with high-temperature gradient adsorption liquid chromatography and CRYSTAF, *J. Appl. Polym. Sci.* 122 (2011) 3211–3217.
- [15] A. Roy, M.D. Miller, D.M. Meunier, A.W. deGroot, W.L. Winniford, F.A. Van Damme, R.J. Pell, J.W. Lyons, Development of comprehensive two-dimensional high temperature liquid chromatography x gel permeation chromatography for characterization of polyolefins, *Macromolecules* 43 (2010) 3710–3720.
- [16] R. Cong, A.W. deGroot, A. Parrott, W. Yau, L. Hazlitt, R. Brown, M. Cheatham, M.D. Miller, Z. Zhou, High temperature thermal gradient interaction chromatography (HT-TGIC) for microstructure analysis of polyolefins, *Macromol. Symp.* 312 (2012) 108–114.
- [17] R. Cong, A.W. deGroot, A. Parrott, W. Yau, L. Hazlitt, R. Brown, M. Miller, Z. Zhou, A new technique for characterizing comonomer distribution in polyolefins: high-temperature thermal gradient interaction chromatography (HT-TGIC), *Macromolecules* 44 (2011) 3062–3072.
- [18] D. Mekap, T. Macko, R. Brüll, R. Cong, A.W. deGroot, A.R. Parrott, Studying binary solvent mixtures as mobile phase for thermal gradient interactive chromatography (TGIC) of poly(ethylene-stat-1-octene), *Ind. Eng. Chem. Res.* 53 (2014) 15183–15191.
- [19] Z. Zhou, M.D. Miller, D. Lee, R. Gong, C. Klinker, T. Huang, C. Li Pi Shan, B. Winniford, A.W. deGroot, L. Fan, T. Karjala, K. Beshah, NMR study of the

- separation mechanism of polyethylene-octene block copolymer by HT-LC with graphite, *Macromolecules* 48 (2015) 7727–7732.
- [20] D. Berek, Separation of parent homopolymers from diblock copolymers by liquid chromatography under limiting conditions of desorption, 2-optimization of experimental arrangement, *Macromol. Chem. Phys.* 209 (2008) 2213–2222.
- [21] D. Berek, Separation of parent homopolymers from diblock copolymers by liquid chromatography under limiting conditions desorption, 1 – principle of the method, *Macromol. Chem. Phys.* 209 (2008) 695–706.
- [22] D. Berek, Separation of parent homopolymers from diblock copolymers by liquid chromatography under limiting conditions of desorption 3. Role of column packing, *Polymer* 51 (2010) 587–596.
- [23] D. Berek, Separation of parent homopolymers from diblock copolymers by liquid chromatography under limiting conditions of desorption 4. Role of eluent and temperature, *J. Sep. Sci.* 33 (2010) 3476–3493.
- [24] D. Berek, T. Kitayama, K. Hatada, H. Ihara, I. Capek, E. Borsig, Liquid chromatography under limiting conditions of desorption IV. Separation of macromolecules according to their stereoregularity, *Polym. J.* 41 (2009) 1144–1151.
- [25] T. Chang, Polymer characterization by interaction chromatography, *J. Polym. Sci. Part B Polym. Phys.* 43 (2005) 1591–1607.
- [26] E. Beaudoin, P.E. Dufils, D. Gignes, S. Marque, C. Petit, P. Tordo, D. Bertin, Polystyrene-block-poly(ethylene oxide) from nitroxide mediated polymerization: detection of minor species by coupled chromatographic techniques, *Polymer* 47 (2006) 98–106.
- [27] M. Jacquin, P. Muller, G. Lizarraga, C. Bauer, H. Cottet, O. Theodoly, Characterization of amphiphilic diblock copolymers synthesized by MADIX polymerization process, *Macromolecules* 40 (2007) 2672–2682.
- [28] W. Lee, D.Y. Cho, T.Y. Chang, K.J. Hanley, T.P. Lodge, Characterization of polystyrene-*b*-polyisoprene diblock copolymers by liquid chromatography at the chromatographic critical condition, *Macromolecules* 34 (2001) 2353–2358.
- [29] D. Mekap, T. Macko, R. Brüll, R. Cong, A.W. deGroot, A. Parrott, P.J.C.H. Cools, W. Yau, Liquid chromatography at critical conditions of polyethylene, *Polymer* 54 (2013) 5518–5524.
- [30] D. Berek, Liquid chromatography of macromolecules at the point of exclusion-adsorption transition. Principle, experimental procedures and queries concerning feasibility of method, *Macromol. Symp.* 110 (1996) 33–56.
- [31] B. Trathnigg, A.A. Gorbunov, Discrimination of block structures in liquid adsorption chromatography of polymers. Simulation and experiment, *J. Chromatogr. A* 1329 (2014) 98–106.
- [32] Y.T. Zhu, J. Ziebarth, T. Macko, Y. Wang, How well can one separate copolymers according to both chemical compositions and sequence distributions? *Macromolecules* 43 (2010) 5888–5895.
- [33] M. Rollet, B. Pelletier, A. Altounian, D. Berek, S. Maria, T.N.T. Phan, D. Gignes, Separation of parent homopolymers from poly(ethylene oxide) and polystyrene-based block copolymers by liquid chromatography under limiting conditions of desorption-1. Determination of the suitable molar mass range and optimization of chromatographic conditions, *J. Chromatogr. A* 1392 (2015) 37–47.
- [34] M. Rollet, B. Pelletier, D. Berek, S. Maria, T.N.T. Phan, D. Gignes, Separation of parent homopolymers from polystyrene and poly(ethylene oxide) based block copolymers by liquid chromatography under limiting conditions of desorption-3. Study of barrier efficiency according to block copolymers' chemical composition, *J. Chromatogr. A* (2016), <http://dx.doi.org/10.1016/j.chroma.2016.07.080>.
- [35] P.D. Hustad, R.L. Kuhlman, D.J. Arriola, E.M. Carnahan, T.T. Wenzel, Continuous production of ethylene-based diblock copolymers using coordinative chain transfer polymerization, *Macromolecules* 40 (2007) 7061–7064.
- [36] C. Li Pi Shan, L.T. Hazlitt, Y.W. Cheung, B.C. Poon, P.D. Hustad, R.L. Kuhlman, E.M. Carnahan, X.H. Qiu, A.N. Taha, Ethylene/*α*-olefin block interpolymers, in: U.S. Patent (Ed.), US 7,608,668 B2, Dow Global Technologies Inc, 2009.
- [37] A. Ginzburg, T. Macko, V. Dolle, R. Brüll, Characterization of polyolefins by comprehensive high-temperature two-dimensional liquid chromatography (HT 2D-LC), *Eur. Polym. J.* 47 (2011) 319–329.
- [38] B.H. Chung, S. Park, T.Y. Chang, HPLC fractionation and surface micellization behavior of polystyrene-*b*-poly(methyl methacrylate), *Macromolecules* 38 (2005) 6122–6127.
- [39] N.A. Lynd, A.J. Meuler, M.A. Hillmyer, Polydispersity and block copolymer self-assembly, *Prog. Polym. Sci.* 33 (2008) 875–893.
- [40] A. Albrecht, R. Brüll, T. Macko, H. Pasch, Separation of ethylene-vinyl acetate copolymers by high-temperature gradient liquid chromatography, *Macromolecules* 40 (2007) 5545–5551.
- [41] D. Lee, C. Li Pi Shan, D.M. Meunier, J.W. Lyons, R. Cong, A.W. deGroot, Toward absolute chemical composition distribution measurement of polyolefins by high-temperature liquid chromatography hyphenated with infrared absorbance and light scattering detectors, *Anal. Chem.* 86 (2014) 8649–8656.