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ORIGINAL

Analytical Solutions for Characterization of the Chemical Composition Distribution of Linear Low-Density Polyethylene: Leveraging Structure Retention Relationships and Relative Energy Density

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Abstract
Ethylene/1-olefin copolymers have held industrial significance for a considerable period. A series of copolymers with identical molar mass and varying 1-hexene levels were synthesized using supported metallocene catalyst. Various analytical techniques were used to characterize the copolymers, focusing on the effect of increasing 1-hexene content on their chemical properties, specifically chemical composition distribution (CCD). Initially, the investigations carried out by differential scanning calorimetry (DSC) revealed broad and asymmetric thermograms with the presence of a distinct shoulder in samples with higher 1-hexene content. Furthermore, HT-GPC with IR5 detector revealed uniform chemical composition (1-hexene concentration) along the molar mass axis. Examination of the chemical composition distribution (CCD) was conducted using two variants of high-temperature liquid adsorption chromatography (HT-LAC), namely solvent gradient interaction chromatography (SGIC) and thermal gradient interaction chromatography (TGIC). Initial testing by employing solvents common to HT-LAC showed that the elution behavior did not correspond with the distinct thermal properties DSC. In the next step, new desorption-promoting solvents were identified using a recent approach that integrates structure retention relationships (SRR), a measure of solvent–stationary phase interactions, with Hansen solubility parameters (HSP), assessing polymer–solvent interactions. The broad and asymmetric CCD in samples with higher SCB, characterized by a main peak and a shoulder, was confirmed by SGIC using newly identified desorption-promoting solvents identified via the SRR–HSP method. This CCD profile was also corroborated by TGIC using a binary solvent mixture as the mobile phase.

Keywords Ethylene/1-hexene copolymers · Liquid adsorption chromatography · Chemical Composition Distribution · Structure retention relationships-Hansen solubility parameters

Introduction

Polyolefins remain the most widely manufactured synthetic polymers globally, with a wide range of uses spanning from medical implants to automotive components and packaging materials [1, 2]. Their versatility can be attributed primarily to their highly customizable properties achieved through advanced catalyst technology which gives precise control of their molecular architecture. Polyolefins produced by the introduction of different comonomers in the backbone broadens the range of properties and thereby end-use applications [1–3]. A specific challenge is the elucidation chemical composition (CC) and chemical composition distribution (CCD) of these copolymers, which is one of the most important structural parameters and is significant for developing structure–property relationships.

Information about the chemical composition (short-chain branching) can be obtained by employing GPC hyphenated with an online filter-based IR detector, which was developed by Ortin et.al. and has been employed in several studies [4, 5]. The model consists of one broad filter to quantify the total absorption of the C–H region and the two narrow filters to measure the absorption of the C–H from the methyl

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groups and C–H from methylene. The ratio of CH_3/CH_2 provides the average short-chain branching for individual molar mass slices along the molar mass axis [4].

Analytical temperature rising elution fractionation (a-TREF) [6, 7] and crystallization analysis fractionation (CRYSTAF) [8] and CEF [9] were among the initial analytical methods to evaluate composition distribution of polyolefins. These techniques separate the polymers according to crystallization of the macromolecules from a hot solution. For ethylene/α-olefin copolymers, the fractionation mechanism is governed by the differences in the crystallization of longest ethylene sequences (LES) in the macromolecules. While the peak elution temperature often shows a linear dependence on the α-olefin molar fraction in a copolymer, the elution curve itself does not directly represent the chemical composition distribution (CCD) [10]. For ethylene/α-olefin copolymers, the shape of the elution curve is instead governed by the length of LES in the polymer chains, which is a complex function of the copolymer's molar mass (MM), α-olefin molar fraction, and the monomer reactivity ratios. Furthermore, factors such as crystallization kinetics and co-crystallization phenomena substantially obscure the already complicated relationship between the experimental elution curves and the CCD [10].

While several polyolefins exhibit semi-crystallinity, polyolefin copolymers with comonomer contents (typically > 3 mol. %) represent polyolefin materials that are primarily amorphous [11]. Consequently, high-temperature liquid adsorption chromatography (HT-LAC), specifically high-temperature solvent gradient interaction chromatography (HT-SGIC) has become the preferred technique that does not rely on the crystallization of polymer chains [12–14].

In HT-SGIC, a solution of the polyolefin sample is pumped through a chromatographic column, typically packed with porous graphitic carbon (PGC) particles as the stationary phase. Initially, the polymer molecules are adsorbed onto the stationary phase from the solution with a solvent that promotes adsorption (adsorli). Subsequently, a solvent gradient is applied by introducing a thermodynamically favorable solvent that supports desorption (desorli) of the macromolecules. This gradual desorption process separates polyolefins based on their chemical composition [12]. For ethylene/1-olefin copolymers, CCD is a key factor influencing their chromatographic behavior [13–15]. Polyolefins like polyethylene and polypropylene were separated for the first time according to chemical composition by HT-SGIC by Macko et.al. They used PGC as the stationary phase in conjunction with solvent gradient of 1-decanol→1,2,4-trichlorobenzene [12]. Since then, it has been applied to characterize the CCD of various polyolefins, such as ethylene/1-alkene copolymers [13], polyolefin plastomers/elastomers [16], and ethylene–vinyl acetate copolymers [17]. It has also been used to separate cyclic olefin copolymers such as ethylene/norbornene having complex microstructures [18].

A related variant of HT-LAC is high-temperature gradient interactive chromatography (HT-TGIC). In TGIC, polyolefins are initially adsorbed onto a PGC surface using a thermodynamically favorable solvent by reducing the temperature. Subsequently, they are desorbed by gradually increasing the temperature. HT-TGIC separates polymer molecules based on their interactions with the PGC surface, which is primarily governed by the SCBD. The first TGIC of polyolefins was realized by Cong et.al. in 2011, wherein they separated HDPE, PP stereoisomers, and ethylene/1-octene copolymers (EO) using PGC and employing ortho-dichlorobenzene (*o*DCB) and 1,2,4- trichlorobenzene (TCB) as mobile phases [19]. In the last decade, several studies have applied TGIC for polyolefin separations [20]. In a study by Ndiripo et al., for the first time, simultaneous application of SGIC and TGIC was realized to separate complex blends of low molar mass polyethylene and ethylene-co-1-octene copolymers [21].

In HT-LAC, the separation and resolution can be limited due to unoptimized experimental conditions which can lead to obscuring certain characteristics of CCD. Arndt et al. explored different solvents to understand their effect on the separation of polyolefins [16]. In the case of polypropylene, HT-SGIC was found to be sensitive to polymer's tacticity, i.e., it enabled the separation of isotactic, syndiotactic, and atactic polypropylene. In this review, Macko et al. concluded that the solvent systems differed in their capability to distinguish stereoisomers, with some being more effective than the others [22]. In addition, studies on HT-SGIC of polyolefins have reported that the desorption-promoting solvents have a stronger influence on improving separation than adsorption-promoting solvents [19, 23]. Mekap et al. conducted a comprehensive study on the use of binary solvent mixtures as mobile phases in TGIC of EO copolymers. They found an increase in the chromatographic resolution by testing with binary mobile phases of varying compositions [24]. In a recent study, solvent selection in LAC of ethylene–propylene diene monomer (EPDM) copolymers was streamlined by combining the solvent–stationary phase interaction in terms of structure retention factor (SRR) and the solvent–polymer interactions (defined by relative energy density, RED) [23]. Thus, solvents play an important role in HT-LAC for characterizing the CCD of polyolefins; however limited knowledge exists on the identification of new mobile phases.

There has been a significant interest in polyolefin materials derived from higher 1-olefins such as 1-butene, 1-hexene, and 1-octene. The materials made from these copolymers have gained industrial success due to their advantageous properties such as high melt flow, increased stiffness, and

reduced crazing [11]. In the case of copolymers made with metallocene catalysts, measuring the CCD could provide insignificant information, because of their simple microstructure, i.e., narrow distribution in terms of both molar mass and chemical composition. However, it was observed that even metallocene catalysts can produce broad and asymmetric CCD, although the polymerization conditions were not reported [16]. In a recent study, it was observed that metallocene catalysts supported on inorganic materials (SiO_2) demonstrated mass-transfer resistance and non-uniform active sites leading to a broad CCD because comonomers cannot access all sites equally [25].

Building on our brief article [26], this work presents an in-depth analysis of the CCD of ethylene/1-hexene copolymers with different comonomer levels, produced via supported metallocene catalysis. We begin by analyzing the samples using differential scanning calorimetry (DSC), later followed by HT-GPC with filter-based IR detector. Subsequently, we employed chemical composition-based separation techniques such as HT-SGIC and HT-TGIC. This study also examines the use of the SRR–HSP method for identification and selection of new mobile phases for LAC [23]. Using results from the SRR–HSP method, we aim to optimize the experimental conditions for HT-LAC to unravel the CCD of the EH copolymers.

Experimental

Polymer Samples

For this study, LLDPE samples of varying 1-hexene content and similar molar mass were produced using a supported metallocene, continuous slurry process at steady state with uniform polymerization conditions.

HT-SGIC

HT-SGIC measurements were done using a prototype instrument (PolymerChar, Valencia, Spain). The mobile phase, injector, and the column were heated to a temperature between 130 and 170 °C depending on the solvent used. Sample concentration of 1–2 mg/mL and a flow rate of 0.8 mL/min were used. A high-temperature Hypercarb™ column (Thermo Fisher Scientific, Dreieich, Germany, 100 mm × 4.6 mm L x I.D.) containing spherical particles of porous graphitic carbon with a diameter of 5 µm, surface area of 120 m^2/g, and pore size of 250 Å was used as the stationary phase. An evaporative light scattering detector (ELSD), model PL-ELS 1000 (Polymer Laboratories, Stretton, UK), was employed. The nebulizer temperature was set to the column temperature; the evaporation temperature was set to 260 °C, and a nitrogen flow rate of 1.5 L/min was maintained. For analysis, three different solvent gradients were programmed in the pump: 0–3 min 0 vol% desorli, 3–13 min (3–23 and 3–33) linear solvent gradient from 0 to 100 vol% desorli, 13–15 min (23–25 and 33–35 min.) 100 vol. % desorli, 15–17 min. (25–27 and 35–37 min) linear gradient from 100 to 0 vol% desorli. To address the question of reproducibility, we performed a multi-run SGIC analysis on a representative sample ($EH_{0.5}$). The resulting standard deviation of the elution volume was found to be ± 0.006 ml. This low variance confirms the good instrumental and methodological reproducibility of the measurements.

HT-TGIC

HT-TGIC measurements were accomplished using a prototype instrument (PolymerChar, Valencia, Spain). The same column was used as in HT-SGIC. Polymer solutions with a concentration of 1–2 mg/mL were prepared by dissolving the samples in the respective mobile phase at 160 °C for 2–3 h. The following temperature and flow method were utilized. Stabilization temperature: 160 °C, final temperature during cooling the process: 50 °C, final temperature during elution process: 175 °C, cooling rate during cooling process: 3 °C/min, heating rate during the elution process: 1 °C/min, flow rate during the cooling process: 0.03 mL/min, flow rate during the elution process: 0.5 mL/min. An evaporative light scattering detector (ELSD), model PL-ELS 1000 (Polymer Laboratories, Church Stretton, England), was used to monitor the analyte. The nebulizer temperature and the evaporation temperature were fixed at 170 and 260 °C, respectively, with a nitrogen flow rate of 1.5 L/min.

High-Temperature Size Exclusion Chromatography (HT-SEC)

HT-SEC measurements were carried out at 160 °C using a PolymerChar GPC-IR (PolymerChar, Valencia, Spain), equipped with a 200 µL sample loop. 1,2,4-Trichlorobenzene (1,2,4-TCB) (Across Organics, Schwerte, Germany) containing 0.5 g/L butylhydroytoluene (BHT, Merck, Darmstadt, Germany) was used as the mobile phase. The flow rate was set at 1 mL/min. Three POLEFIN linear XL analytical columns, 300 × 8.0 mm (Polymer Standards Service, Mainz, Germany), were used as the stationary phase. A filter-based multiple band IR detector (model IR5-MTC, PolymerChar, Valencia, Spain) featuring a thermoelectrically cooled mercury–cadmium–telluride (MCT) sensor was used for detection. The IR5 detector has two narrow band filters tuned to the adsorption region assigned to the CH_3 (at 2960 cm^{-1}) and CH_2 (2920 cm^{-1}) groups, as well as a broader filter used to collect absorbance from all C–H bonds in the analyte.

DSC

A Mettler Toledo DSC 822e instrument was used for measurement. A temperature sweep was carried out between −50 °C and 150 °C with a heating/cooling rate of 5 K/min and a hold time of 5 min at each temperature. Melting and crystallization temperatures were taken from the second heating and cooling cycle.

Solvents

Toluene, xylene isomers, 1,3,5-trimethylbenzene (1,3,5-TMB), ethylbenzene (EB), diethylbenzene, (DEB), *n*-propylbenzene (PB), butylbenzene, amylbenzene, hexylbenzene, heptylbenzene, octylbenzene, nonylbenzene, decylbenzene. isopropylbenzene (IB), tert-butylbenzene (TB), chlorobenzene (CB), 1,3-dichlorobenzene (*m*DCB), 2-chlorotoluene (2-CT), 4-chlorotoluene (4-CT), tetralin, 1-chloronaphthalene (1-CN), 1,2,4-trimethylbenzene (1,2,4-TMB), 1,2,3-trimethylbenzene (1,2,3-TMB), nitrobenzene, benzaldehyde, phenol, anisole, diphenylmethane, benzonitrile, diphenyl ether, methanol, n-decane, and 1-decanol were used as received. 1,2-Dichlorobenzene (*o*DCB) and 1,2,4-TCB (for synthesis, Merck, Darmstadt, Germany) were distilled prior to use.

Results and Discussion

DSC

The EH copolymer samples with varying SCB contents were probed using DSC to analyze their thermal properties. Their thermal profile is shown in Fig. 1a (second heating). The relation between SCB per 1000 total carbon atoms and peak melting/crystallization temperature (T_m/T_c) is shown in Fig. 1b. A brief overview of the properties is provided in Table 1. The degree of crystallinity was evaluated from the calculated enthalpies of crystallization using the literature value for polyethylene with 100% crystallinity of 293 J/g [27]

Several important observations can be made from Fig. 1 and Table 1. Both the thermal transition temperatures (melting and crystallization), % crystallinity, and density decrease as the comonomer content increases. These observations are consistent with the effect of comonomer content (SCB) on the thermal and bulk properties of copolymers. It can be observed that the second heating thermograms of all samples are broad and asymmetrical. It has been reported that supported metallocene-catalyzed LLDPE copolymers show

Table 1 Overview of SCB content (NMR), weight average molar mass (M_w), and dispersitiy (Đ) as calculated from HT-SEC

Sample name	SCB (per 1000 total carbon atoms)	M_w (kg/mol)	Đ
	(NMR)	SEC-IR	SEC-IR
$EH_{12.7}$	12.7	142	2.6
$EH_{11.2}$	11.2	143	2.7
$EH_{8.6}$	8.6	146	2.6
$EH_{5.1}$	5.1	145	2.7
$EH_{4.0}$	4.0	144	2.8
$EH_{2.6}$	2.6	141	2.7
$EH_{0.8}$	0.8	141	2.7
$EH_{0.5}$	0.5	142	2.8

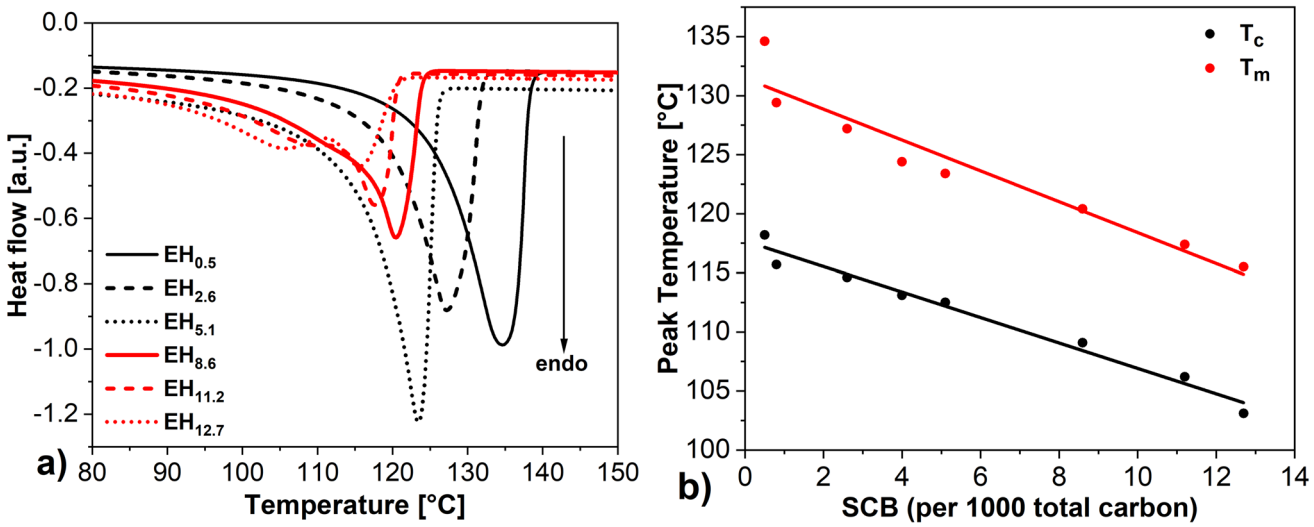

Fig. 1 **a** DSC second heating profiles at a heating rate of 5 K/min. **b** Correlation between T_m/T_c and SCB per 1000 total carbon atoms

broadening of endotherms and even two melting events in DSC investigations. The broadening of endothermic can be attributed to factors such as diverse crystal sizes, broad MMD, and/or differences in thermal histories [28, 29]. As all the samples were prepared in a similar way and the DSC measurements were realized at the same conditions, the influence of thermal history on the observed differences can be eliminated. Since the MMD of the samples are the same (Table 2 and Fig. S1 in SI), its influence can also be neglected. One possibility can be attributed to the disruption of lamellar crystal formation caused by the incorporation of 1-hexene comonomer as short-chain branches, which act as defects that are excluded from the crystalline domains and confined to the amorphous phase.

Another observation is that the thermograms of samples with lower SCB content show only one clearly distinguishable melting peak. In samples with higher SCB content, ($EH_{11.2}$) and ($EH_{12.7}$), the heating curves show a very distinct shoulder representative of two distinct populations (melting events). Similar features were observed for the second cooling cycle i.e., broad and asymmetric curves for all samples with shoulder for $EH_{11.2}$ and $EH_{12.7}$. This observation is not unexpected, as according to Stockmayer distribution theory, copolymers containing higher 1-hexene content exhibit broader CCD and greater heterogeneity in crystallizable ethylene sequence lengths. Since DSC is sensitive to all crystallizable sequences (both inter- and intramolecular), this results in broader melting endotherms compared to the more selective fractionation techniques such as a-TREF, CEF, and CRYSTAF, which primarily respond to intermolecular compositional variations [30]. Czaja et al. reported that DSC analysis of EH copolymers synthesized using a supported zirconocene catalyst showed peak broadening with increasing 1-hexene content, and in some cases, the appearance of two distinct melting peaks [29]. Similarly, Arndt et al. observed similar thermal profiles in EO copolymers with higher SCB content prepared using metallocene catalysts. They hypothesized that the samples may exhibit a broad CCD, indicative of intermolecular heterogeneity given the close correlation between SCB content and melting/crystallization temperature [16]. Similar conjecture can be drawn at this stage, but further analytical characterization is required to determine the CCD of the samples.

Table 2 Overview of SCB content (NMR), crystallization (T_c) and melting temperature (T_m) and estimated % crystallinity from DSC data

SCB (per 1000 total carbon atoms)	T_c (°C)	T_m (°C)	% crystallinity	Density
0.5	118.2	134.6	63.8	0.9503
0.8	115.7	129.4	56.3	0.9418
2.6	114.6	127.2	54.9	0.9381
4.0	113.1	124.4	50.5	0.9342
5.1	112.5	123.4	49.8	0.9318
8.6	109.1	120.4	46.1	0.9252
11.2	106.2 (97.33)	117.4 (107.9)	43.7	0.9209
12.7	103.1 (94.5)	115.5 (105.2)	40.0	0.9174

T_c and T_m values in bracket correspond to shoulder. Density is determined via samples being molded according to ASTM standards (ASTM D4703; Annex A1, Procedure C) and measured using a gradient column (ASTM D1505)

HT-GPC-IR

Measuring the SCB distribution along the molar mass axis offers additional insights into the sample's chemical structure beyond conventional GPC. This may be critical when dealing with samples that have very similar MMDs, such as the EH copolymers in this study, but potentially different comonomer incorporation. Uniform comonomer incorporation is a characteristic of unsupported metallocene-catalyzed samples [31]. Since the copolymers in our study were synthesized using a supported metallocene catalyst, it is of interest to investigate potential differences in comonomer incorporation given the observations made in DSC measurements. By analyzing EH copolymers by GPC with the addition of composition signal, i.e., IR, it is possible to see differences in their comonomer distributions. In Fig. 2, SCB (CH_3/CH_2) along the MMD curve is shown for $EH_{2.6}$ and $EH_{11.7}$.

As shown in Fig. 2, the two edges of the peaks exhibit scattered CH_3/CH_2 values due to the low signal intensity (less quantity of material) in these regions. An approach was developed by Ortin et al., to estimate confidence in the determination of SCB per 1000 total carbon atoms along the MM axis. They used pipe-grade HDPE resin as an example and found that the minimal required concentration at the detector cell was 0.009 mg/mL, for an estimated error of one unit of CH_3/1000TC [32].

The two samples clearly exhibit similar MMDs and homogeneous incorporation of 1-hexene across the MM. Uniform distribution of SCB is present in all the EH copolymers. It is concluded that compositional heterogeneity is not correlated with the polymer's MM based on the similar MMDs and homogeneous 1-hexene incorporation across the molar mass axis. To investigate potential compositional heterogeneity as implied in DSC, the samples were further analyzed using chemical composition-based separation techniques, namely HT-TGIC and HT-SGIC.

HT-LAC

ELSD was selected for HT-TGIC measurements primarily for practicality and system compatibility, as a suitable composition-sensitive IR detector was not readily integrable with

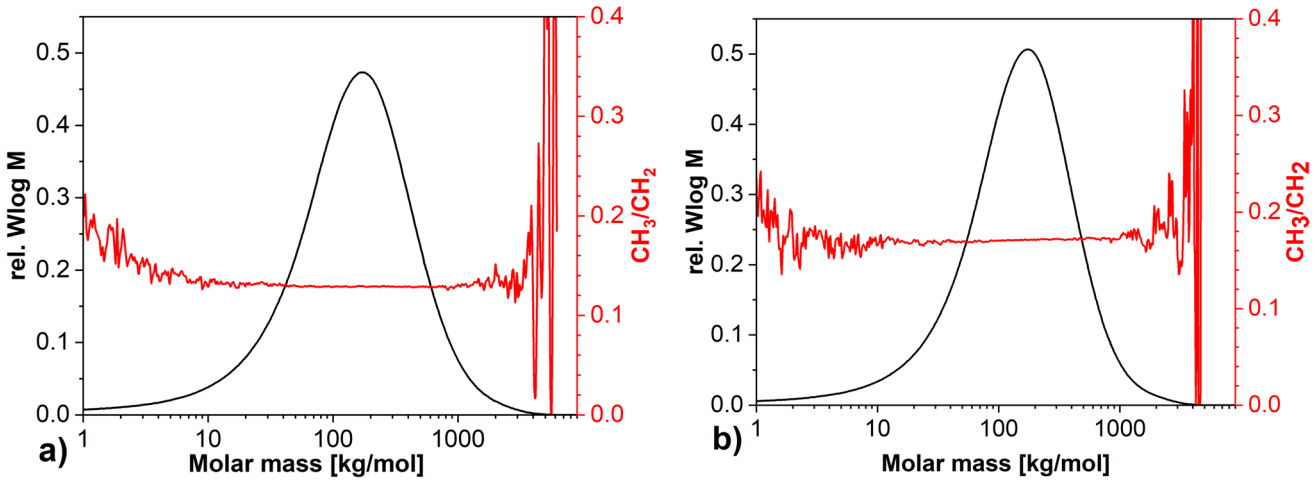

Fig. 2 Molar mass distribution (black solid curve) and SCB distribution (red solid line). **a** $EH_{2.6}$; **b** $EH_{11.2}$

the existing HT-LAC system. The response of ELSD detectors has been the subject of many investigations. It is known for its inherently non-linear response and dependence on particle size/morphology might influence the precise shape and quantitative interpretation of the perceived CCD profile compared to a composition-sensitive and potentially more linear detector like IR [33]. Figure 3 shows the separation achieved by TGIC using commonly employed single-solvent mobile phase method.

As observed in Fig. 3, as the SCB content increases, the elution temperature (T_e) decreases ($EH_{11.2}$ elutes at a lower T_e compared to $EH_{5.6}$). In TGIC, T_e is associated with the desorption of polymer chains from the stationary phase. An increase in SCB content reduces the interactions of the macromolecules with the PGC surface, resulting in faster desorption and thus lower T_e. It can be observed that *o*DCB has lower desorption strength compared to TCB based on the higher range of T_e of samples with the former. By using 1,2,4-TCB or *o*DCB, the chromatograms do not suggest the presence of CCD main peak with a shoulder in samples with higher SCB content. To further probe the CCD, the samples were separated using SGIC.

A common approach for SGIC is a 10 min solvent gradient, adsorli → desorli, which was initially chosen. The adsorli was changed from n-decane to 2-ethyl-1-hexanol (2-EH) while keeping the desorli (1,2,4-TCB) constant, followed by varying the desorli to *o*DCB while keeping the adsorli (n-decane) unchanged. An overlay of chromatograms is shown in Fig. 4.

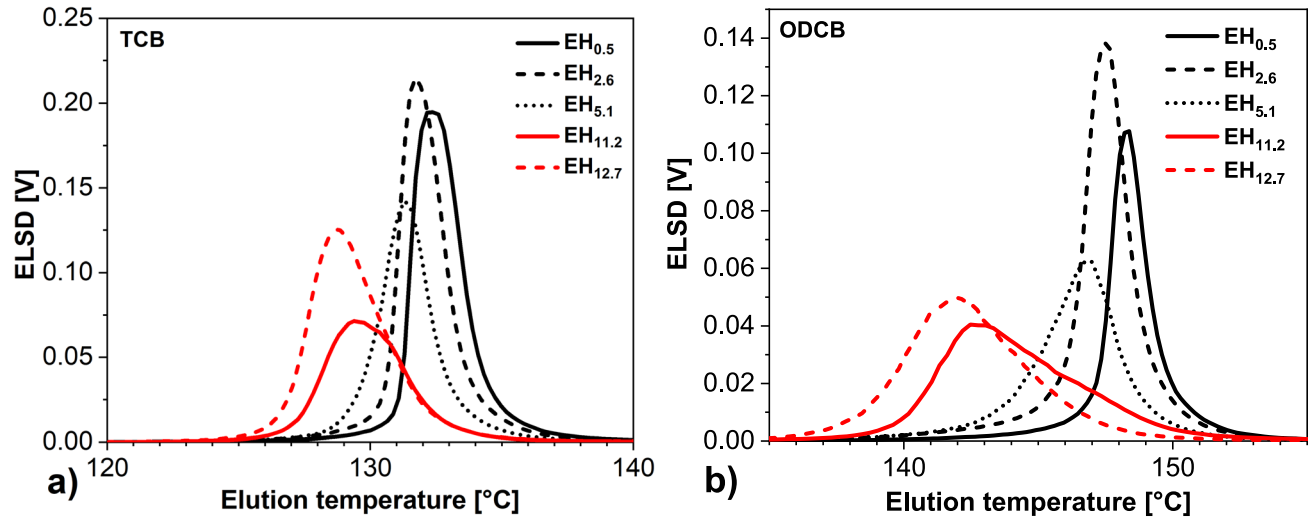

Fig. 3 TGIC separation using single eluent mobile phase. **a** 1,2,4-TCB; **b** *o*DCB

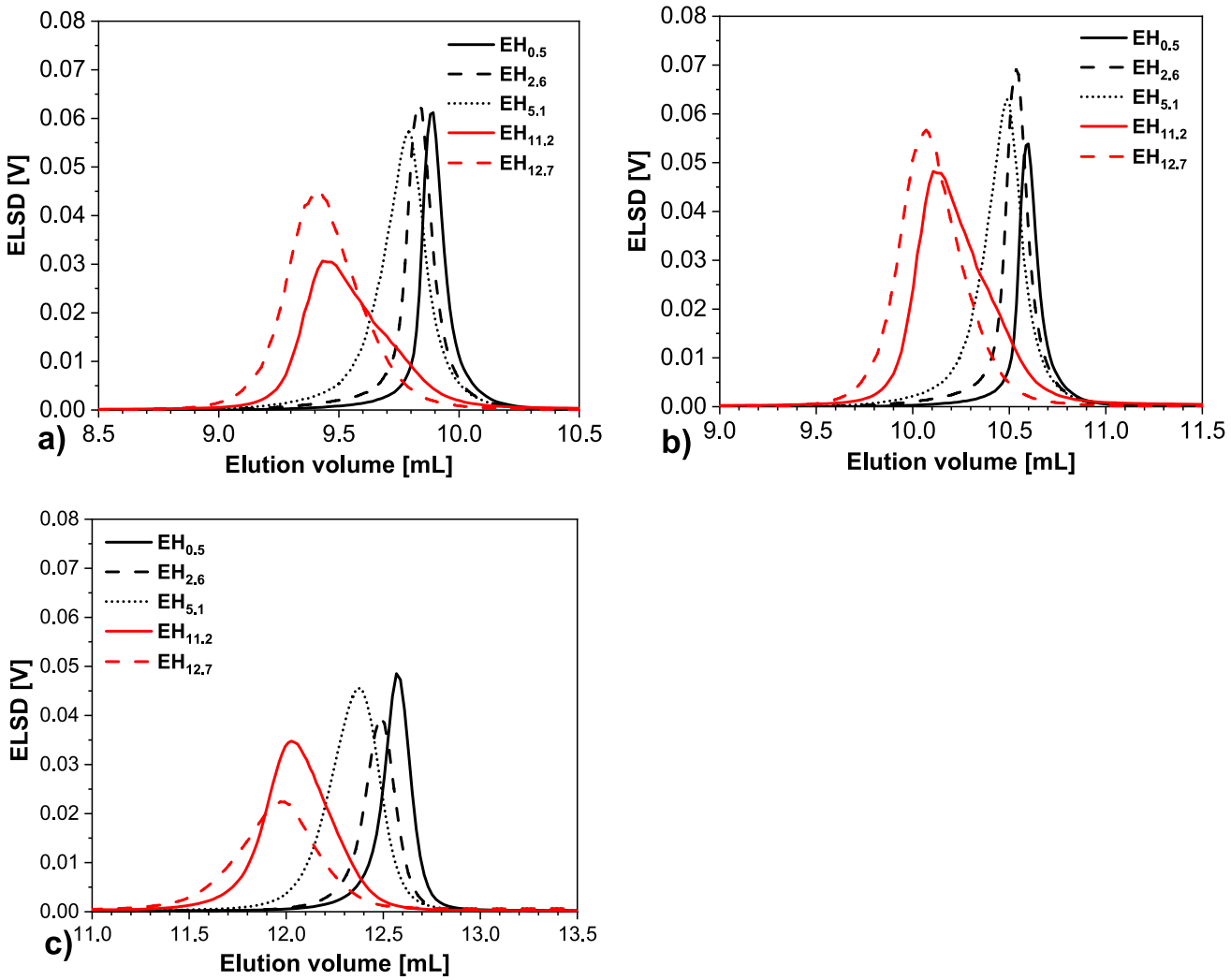

Fig. 4 Overlay of chromatograms using different solvent systems; **a** *n*-decane→1,2,4-TCB; **b** 2-EH→1,2,4→TCB; and **c** *n*-decane→*o*DCB. Solvent gradient is 10 min at 160 °C

The elution volume (V_e) of samples decreased with increasing SCB content for all the solvent systems. This is because the short-chain branches hinder the adsorption of polymer chains on the PGC surface and hence less desorli is required for eluting the samples, thus leading to lower V_e. In Fig. 4a, b (different adsorlis), no indication of the previously observed shoulder in CCD is noticeable for higher SCB samples. Hence, the changes in the adsorli do not play a major role in improving separation as well as the resolution, which has been documented in other investigations [16, 23]. As shown in Fig. 4a, c, different desorption-promoting solvents were used. Employing 1,2,4-TCB and *o*DCB as desorlis did not provide direct evidence of a CCD with shoulder. *o*DCB was chosen as a desorli because it has weaker desorption strength and thus generally provides better separation as previously reported [34].

At first instance, this suggests that the distribution of comonomer units within the polymer chains is probably unimodal which is consistent regardless of the solvent system. Previous investigations on SGIC of PO's and PO elastomers have reported that changing the desorli has a greater impact on separation than altering the adsorli [16, 23]. Similarly, Mekap et al. reported that by varying the desorption-promoting capability of the mobile phase, the resolution of TGIC-based separations can be maximized [24]. Herein, they optimized binary solvent mixtures that enabled an improvement in resolution. At this stage, optimizing the experimental conditions would be the initial point to elucidate the CCD characteristics. Therefore, it is essential to explore alternative solvents that can serve as desorlis (or mobile phases in TGIC) which exhibit weaker desorption strength than chlorinated candidates.

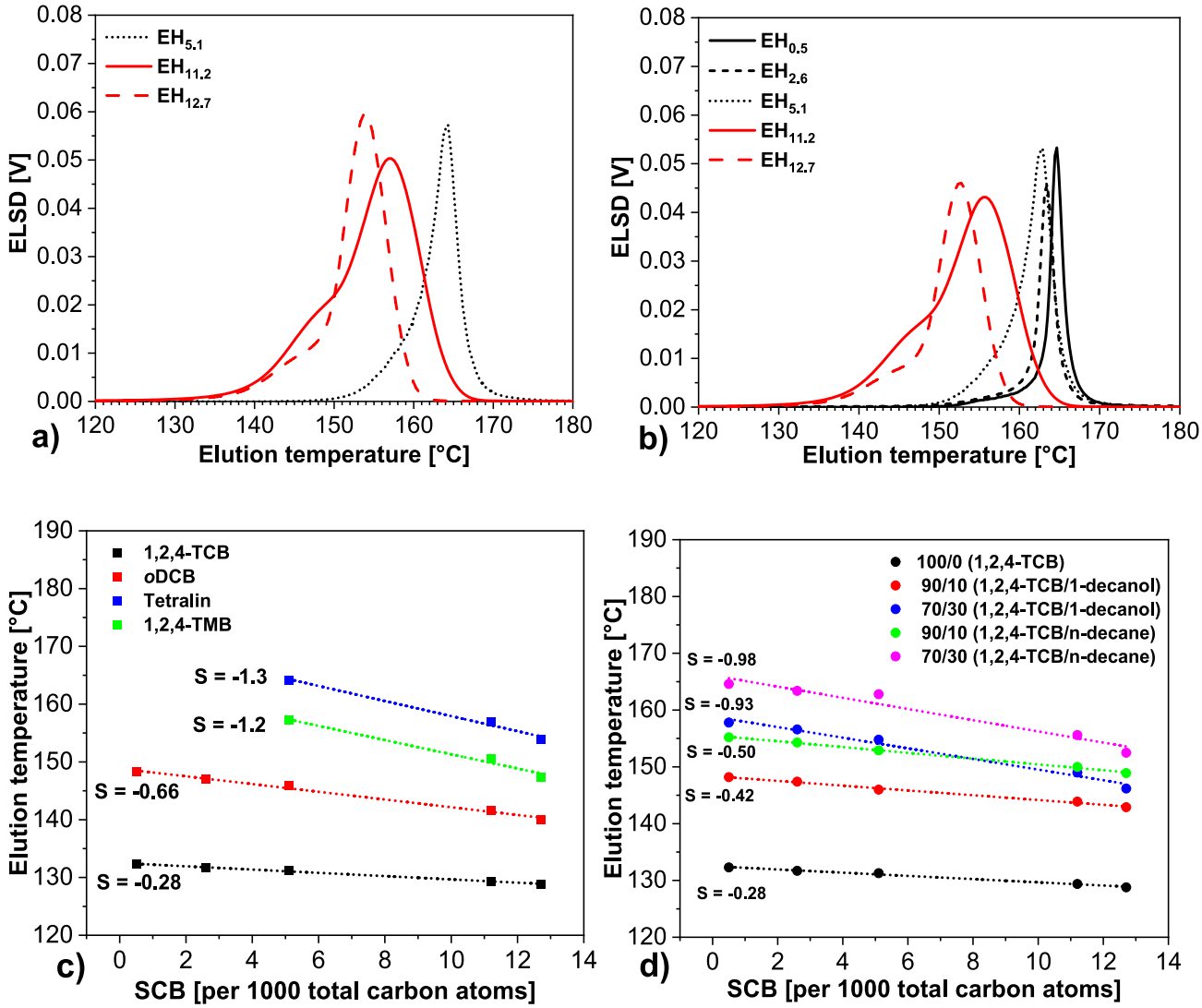

Fig. 5 TGIC separation of EH copolymers using different mobile phases. **a** Tetralin; **b** 70/30 (v/v) 1,2,4-TCB/n-decane; **c** T_e vs SCB for single-solvent mobile phases; and **d** T_e vs SCB for 1,2,4-TCB/n-decane binary mobile phase combinations

Solvent Selection for TGIC and SGIC

Building on our previous investigation concerning solvent selection for LAC of EPDM, solvents were classified as either adsorlis or desorlis based on their interaction strength with the PGC [23]. Solvents exhibiting stronger interactions with the stationary phase reflected by higher retention volume (retention factor, log k) were designated as desorlis, while those with weaker interactions (lower retention factor) were categorized as adsorlis. In short, the retention volume of the tested solvents was determined by injecting them in methanol mobile phase onto the PGC stationary phase. This approach was extended to facilitate the identification of new solvents for both TGIC and SGIC of EH copolymers.

A structure retention relationships (SRRs) and Hansen solubility parameters (HSPs) plot was developed for a series of solvents and an illustrative LLDPE copolymer (Fig. S2 in SI). According to this plot, solvents that fit into the following criteria, namely, log $k < \log k_c$ and relative energy difference (RED < 1), are generally classified as adsorlis (bottom left region), whereas those with log $k > \log k_c$ and RED < 1 are grouped as desorlis (top left region). Here, k_c represents the critical retention factor that distinguishes adsorlis from desorlis. This value can be estimated empirically based on HPLC studies of LLDPE copolymers, although the precise value of k_c is not important to this study. RED is correlated with the interactions between the polymer and solvent (solubility). The RED for a solvent–polymer combination was obtained from the HSP values, and log k for

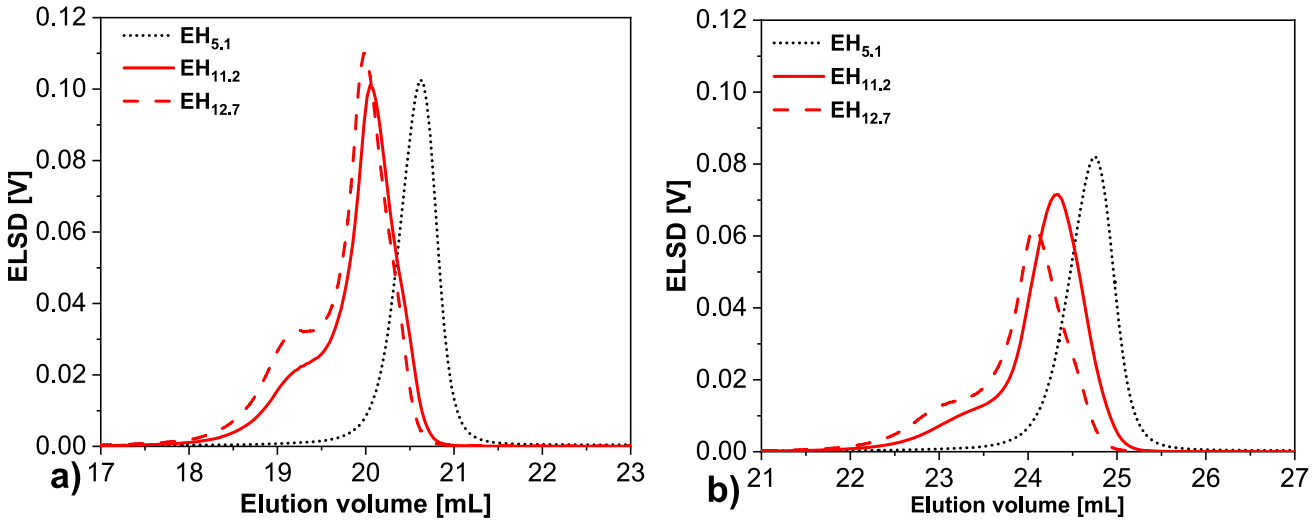

Fig. 6 Overlay of chromatograms using different desorption-promoting solvents (desorli) and 30 min solvent gradient, 170 °C; **a** *n*-decane→1,2,4-TMB; **b** *n*-decane→tetralin

the solvent–stationary phase was calculated according to the procedure described previously [23].

HT-LAC Using the SRR–HSP

For the single-solvent mobile phase approach, 1,2,4-trimethylbenzene (1,2,4-TMB) and tetralin were selected as mobile phases for HT-TGIC because their log k values are comparable to chlorinated desorlis (ex. *o*DCB and *m*DCB) and they differ significantly from chlorinated solvents such as 1,2,4-TCB and 1-CN (Fig. S2, SI). While selecting a single solvent as the mobile phase for improving the resolution, it is rational to assume that its retention factor should be between a strong desorli and a strong adsorli. On one hand, the selected solvent candidates should not promote excessive polymer adsorption (low log k), or else the macromolecules might be adsorbed on the stationary phase too strongly to elute in a reasonable time. On the other hand, the solvents should not suppress interactions excessively (high log *k*), otherwise, the analyte might elute with poor resolution which essentially defeats the purpose of this study.

In the binary solvent mixture method, a combination of a solvent with high log k (desorli) and a solvent with low log *k* (adsorli) was employed to enhance resolution, which was not possible using either 1,2,4-TCB or *o*DCB (Fig. 3). *n*-Decane was selected as the solvent to promote the adsorption, whereas 1,2,4-TCB was chosen as a solvent to facilitate desorption. By varying their ratio, the overall elution strength of the isocratic mobile phase was modified. Using this approach of varying solvent strength, the elution behavior of EH copolymers was measured in binary mixtures of 1,2,4-TCB with *n*-decane. By using the SRR–HSP plot (Fig. S2, SI), different solvent combinations with high and low retention factors can be identified and selected.

EH samples were separated using the above single-solvent mobile phase system (tetralin, Fig. 5a) and binary solvent mixture as TGIC mobile phase (Fig. 5b). T_e as a function of SCB for different single-solvent mobile phases (Fig. 5c) and binary solvent mixture (Fig. 5d) are demonstrated below.

In Fig. 5a, using tetralin as the mobile phase, a shoulder can be observed for $EH_{11.2}$ and $EH_{12.7}$ copolymer samples. The use of tetralin also resulted in incomplete desorption of samples with lower SCB, likely due to their limited ability to promote desorption (lower log *k*). As evidenced by Figs. 3a, b and 5a, c, the $T_{e,}$ values of the EH copolymers are lowest in 1,2,4-TCB compared to *o*DCB, 1,2,4-TMB and tetralin which is in alignment with the former's stronger desorption-promoting strength (c.a. Fig. S2 in SI). For the binary mobile phase method, when the amount of the adsorption-promoting solvent is increased, at a specific mobile phase composition, 70/30 (v/v) 1,2,4-TCB/*n*-decane, a shoulder appears in the chromatograms of $EH_{11.2,}$ and $EH_{12.7}$ (Fig. 5b). This is in contrast with Fig. 3a where 1,2,4-TCB was used as the mobile phase.

The slope in Fig. 5c, d reflects the difference in T_e for the EH copolymers, which increases with decrease in desorption-promoting capability of the mobile phase, i.e., switching to 1,2,4-TMB, tetralin, or adding n-decane (or 1-decanol) to 1,2,4-TCB. It can be hypothesized that this is a result of improved selectivity of the graphitic surface in differentiating polymer molecules with different chemical structures, driven by modulations in mobile phase composition. In summary, the TGIC investigations confirm the presence of a shoulder in the CCD. In the next step, the samples were

separated using SGIC using the non-chlorinated desorlis and employing a longer solvent gradient as shown in Fig. 6.

Application of 1,2,4-TMB and tetralin as desorlis led to very strong adsorption of the samples with lower SCB content and thus no peaks were observed which corroborates the TGIC results. By using 1,2,4-TMB and tetralin as desorlis along with the longer 30-min solvent gradient, distinct shoulders were observed in the chromatograms of samples with higher SCB. The elution volume of the main peak and shoulder represents their respective comonomer content. The chromatogram was deconvoluted (Fig. S3, SI) and the SCB content was calculated using the calibration (Fig. S4, SI). For $EH_{12.7}$ the SCB values for the main peak and shoulder are 8.9 and 13.9 (9.4 and 14.8 from DSC) and for $EH_{11.2,}$ they are 7.7 and 12.8 (8.5 and 13.4 from DSC), respectively. It can be hypothesized that the deviation of HT-SGIC from DSC is related to the fundamental differences in the principles governing these techniques. DSC measures the thermal transitions associated with crystallizable ethylene sequences, thereby reflecting the distribution of crystallizable segment lengths rather than the true compositional heterogeneity. HT-SGIC separation is driven by polymer-stationary phase interactions which is correlated to the comonomer content (SCB) and represents the CCD of the copolymer.

The use of non-chlorinated desorlis combined with a longer solvent gradient time successfully demonstrated the influence of solvent choice on the shape of the elution profiles, enabling the observation of a main peak and a shoulder in the higher SCB samples.

Conclusions

In this study, LLDPE copolymers with varying amounts of 1-hexene (SCB) content were analyzed using different analytical techniques. Initial investigation using DSC revealed thermograms that displayed distinctive shoulders for samples with higher 1-hexane content. Given that the EH copolymers were synthesized using metallocene catalysts, this was hypothesized to indicate intermolecular heterogeneity (non-uniform incorporation of 1-hexene among different polymer chains) rather than intramolecular variation. Further examination by GPC with filter-based IR detection revealed that the samples had homogenous SCB incorporation along the MMD based on the CH_3/CH_2 ratio. Chemical composition-based separation techniques were employed to characterize the potential heterogenous nature of CCD.

The samples were analyzed by both TGIC and SGIC for characterizing the CCD. Initial measurements by TGIC applying commonly used chlorinated 1,2,4-TCB or *o*DCB as the mobile phase, did not suggest the presence of broad and asymmetric CCD. Furthermore, the samples were separated using SGIC. However, neither the change in adsorli nor in desorli revealed the broad and asymmetric CCD with a distinct shoulder observed in the higher SCB samples. At this stage, alternative solvent candidates were identified using a method that exploits information about the Hansen solubility parameters (polymer–solvent interactions) and structure retention relationships (solvent–stationary phase interactions). These solvents function as desorlis (mobile phases in TGIC) and exhibit poor desorption strength compared to 1,2,4-TCB or 1-CN. In TGIC separation, the use of tetralin and binary mobile phase mixtures of desorli/adsorli lead to an improvement in chromatographic separation. This demonstrated that using 1,2,4-TMB and tetralin as desorlis is effective in maximizing chromatographic resolution leading to elution profiles with a main peak and a shoulder that mimic the bimodal thermal characteristics observed in the DSC thermograms for samples with higher SCB content.

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Data Availability Data generated during the current study is available on reasonable request.

Declarations

Conflict of Interest The authors declare no competing interests.

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