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Improving chromatographic separation of polyolefins on porous graphitic carbon stationary phases: effects of adsorption promoting solvent and column length†

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The chromatographic separation of complex polyolefins on porous graphitic carbon stationary phases is strongly influenced by the composition of the mobile phase. Of particular interest is the effect of the chemical structure of the adsorption promoting solvent as this component of the mobile phase determines the adsorption–desorption behavior of the polyolefin molecules. In a systematic study, alkyl alcohols and linear alkanes are used as adsorption promoting solvents and the effect of the molecules' carbon chain length on chromatographic resolution is investigated. As representative examples, solvent gradient interaction chromatography experiments on polypropylene stereoisomers and ethylene-*co*-1-octene copolymers are presented. In a further study, the effect of increasing chromatographic column length on the solvent gradient separation of ethylene-*co*-1-octene copolymers is investigated. In summary, it is shown that the polypropylene stereoisomers are retained in 1-octanol as well as in *n*-decane and *n*-dodecane, allowing for identification of the individual stereoisomers in complex blends. For ethylene-*co*-1-octene copolymers it is shown that separation improves with increasing carbon chain length of the adsorption promoting solvent. Maximum resolution is obtained when a column length of 300 mm is used with 1-dodecanol as the adsorption promoting solvent.

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Introduction

The need for a better understanding of polymer microstructures necessitates the development and testing of robust advanced analytical techniques and the investigation of complex polyolefins is no exception. Interaction chromatography (IC) techniques for chemical composition separation of polyolefins have been introduced less than two decades ago.[1–3] Fundamentally, such separations must be carried out at high temperatures above the materials' melting temperature (typically above 100 °C) to keep the semicrystalline polyolefin macromolecules in solution. The discovery of porous graphitic carbon (PGC) as a stationary phase for the separation of polyolefins according to chemical composition significantly improved such separations as compared to silica or other stationary phases.[4] On PGC, the interactions of the polyolefin molecules with the substrate (stationary phase) based on adsorptive forces are considered to be more dominant than *e.g.* crystallization or solubility effects. Accordingly, separations of polyolefins can be achieved irrespective of crystallizability, which gives IC significant advantages over conventional crystallization-based techniques such as temperature rising elution fractionation (TREF) and crystallization analysis fractionation (CRYSTAF) which do not work for amorphous samples.[5]

Complementary to solvent gradient IC (SGIC), temperature gradient interaction chromatography (TGIC) has been introduced by Cong *et al.*[6,7] TGIC has several advantages as compared to SGIC which include the use of an isocratic solvent as the mobile phase. This enables the use of multiple detectors thereby providing detailed information on the sample microstructure, *e.g.* on chemical composition and macromolecular dimensions, if infrared (IR) and multiangle laser light scattering (MALLS) detectors are used. On the other hand, SGIC offers better resolution, shorter run times, and a larger separation range in the case of non-crystallizing copolymers.[5] The obvious drawback is the limitation of the number of detectors that can be used for SGIC purposes. In this case *e.g.* infrared detectors are of limited use due to the non-transparent nature of adsorption promoting solvents such as 1-decanol or decane. In such cases, the evaporative light scattering detector (ELSD) becomes the detector of choice.

Similar to other chromatographic approaches, there is a constant drive to improve the separation and resolution capabilities of existing IC techniques.[8–12] In SGIC, a linear gradient is

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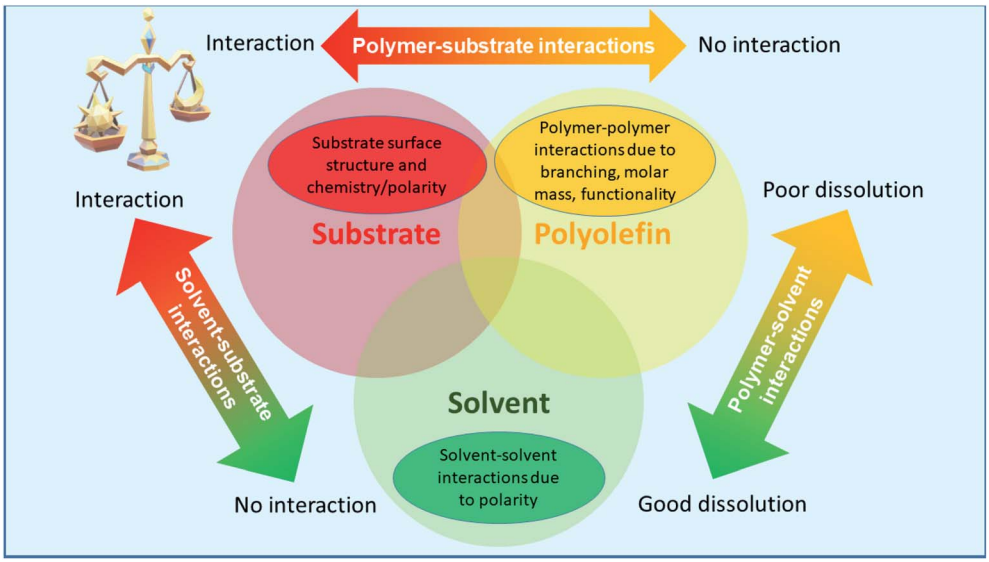

Fig. 1 Schematic diagram showing the complex relationship between solvent, polyolefin sample and stationary phase.

typically applied over a known volume or time at a specific flow rate. These conditions are easy to manipulate and are not strenuous on the chromatographic heating system. Longer gradients have been applied to improve separation.[9,13,14] These are obtained by simply increasing the time required for a linear gradient (adsorption promoting solvent → desorption promoting solvent) to complete the separation at a given flow rate. Another route is to use weaker desorption promoting solvents and in the case of polyolefins, 1,2,4-trichlorobenzene (TCB) has been replaced by 1,2-dichlorobenzene (ODCB).

The complex relationship between the polyolefin sample (its molar mass, composition and molecular topology), the solvent/mobile phase and the substrate (stationary phase) is summarized in Fig. 1. Establishing or improving existing chromatographic techniques for the separation of a polyolefin must be done with the three fundamental parameters in mind. For example, the solvent or mobile phase must be able to dissolve all polymer components by weakening inter- and intramolecular polymer–polymer interactions. On the other hand, the solvent must allow for the polymer chains to adsorb onto the stationary phase to prevent immediate elution after injection. In addition, the solvent choices for a solvent gradient must consider the solvent–substrate interactions. Solvent molecules can compete with the polyolefin molecules for adsorption sites leading to very weak adsorption of the polymer and very strong adsorption of the solvent molecules. At present, there is no approach for determining a suitable solvent gradient that satisfies all prerequisites. Several solvents must typically be tested, given that they must also satisfy other conditions such as having high boiling points and good thermal stability. A fourth condition that must be fulfilled for polyolefin separation is high operating temperature, and temperatures as high as 160 °C have been used previously.[1,2,5,9,10,13–18]

The evaporative light scattering detector (ELSD) is the most frequently used detector for solvent gradient elution separations with the PL-ELS 1000 model being applied for most high temperature work.[1–5,8–10,13,15–21] Several studies have been devoted to the understanding of the ELSD operation,[8,22–24] however, not much is available on detectors used for polyolefin characterization at high temperature. In our previous work,[21] it was emphasized that the optimum operating conditions must be established for each solvent system. The operating conditions and parameters include the nebulizer gas flow and evaporator temperature. Some more detailed considerations on the PL-ELS 1000 maintenance are presented in the ESI.†

As previously mentioned, significant attempts have been directed at obtaining solvent gradient systems and conditions that improve separation and chromatographic resolution of polyolefins. However, these studies were mainly phenomenological using a variety of solvent systems but not specifically focusing on the effect of the chemistry/nature of the adsorption promoting solvent. Typically, similar PGC columns with column lengths of 100 mm were used and the effect of the column length was not studied in detail. In SGIC of polyolefins, the adsorption promoting solvent is crucial in the initial interaction of the injected polyolefin with the substrate (PGC) upon injection. Although several solvents have been compared previously,[10,18,25] the vast differences in the type, polarity and structure of the solvents have not been addressed.

In the present study, linear alkyl alcohols (C8, C10, C11 and C12) and alkanes (C10, C12 and C14) are systematically investigated as adsorption promoting solvents in the SGIC separation of PP stereoisomers and LLDPEs with 0.6–14.0 mol% of 1-octene. The effects of polarity and alkyl chain size of the adsorption promoting solvent on the separation and resolution of PP and LLDPE is thereby studied. In addition, the effect of PGC column length on separation and resolution is systematically investigated.

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Experimental

Materials and solvents

Three PP stereoisomers (iPP, aPP and sPP) were obtained from Sigma-Aldrich, South Africa, and used as received. Ethylene-*co*-1-octene copolymers with comonomer contents of 0.6–14.0 mol% were kindly provided by Borealis Polyolefine GmbH (Linz, Austria). 1-Octanol (>99%), 1-decanol (≥98%), 1-undecanol (≥99%), 1-dodecanol (≥98%), *n*-decane (≥99%), *n*-undecane (≥99%), *n*-dodecane (≥99%), *n*-tetradecane (≥99%) and 1,2,4-trichlorobenzene (>99%) were obtained from Sigma-Aldrich South-Africa and used as received.

Molar mass analysis

Polystyrene equivalent molar masses and dispersities of the samples were determined on a PL-GPC 220 high-temperature chromatograph (Polymer Laboratories, Church Stretton, UK, now Agilent Technologies) equipped with a differential refractive index (RI) detector. The samples (4 mg) were dissolved in 2 mL of TCB for 2 h together with 0.025% BHT which acted as a stabiliser to prevent sample decomposition/degradation. TCB with 0.0125% BHT was used as the mobile phase at a flow rate of 1 mL min^{-1}. Three 300 mm × 7.5 mm i.d. PLgel Olexis columns (Agilent Technologies, UK) were used together with a 50 mm × 7.5 mm i.d. PLgel Olexis guard column. 200 μL of each sample solution was injected. All experiments in HT-SEC were carried out at 150 °C. The instrument was calibrated using narrowly distributed polystyrene standards (Agilent Technologies, UK).

Solvent gradient interaction chromatography

Solvent gradient interaction chromatography experiments were done on a Polymer Char HT-2D-LC instrument (Valencia, Spain), comprising of an autosampler, two separate ovens, switching valves and a high-pressure binary pump equipped with a vacuum degasser (Agilent, Waldbronn, Germany). The main oven was used to accommodate the porous graphitic carbon (PGC) column. The injector and switching valves are located in the second oven and kept at 160 °C. The autosampler is a separate unit connected to the injector through a heated transfer line.

An evaporative light scattering detector (ELSD, model PL-ELS 1000, Polymer Laboratories, Church Stretton, England) was used with the following parameters: gas flow rate 1.5 L min^{-1}, nebuliser temperature of 160 °C, evaporator temperature of 270 °C. A PGC column (Hypercarb®, Thermo Scientific, Dreieich, Germany) with the following parameters: 10–300 mm length and 4.6 mm i.d., packed with porous graphite particles with a particle diameter of 5 μm, a surface area of 120 m^2 g^{-1} and a pore size of 250 Å.

The flow rate of the mobile phase was 0.5 mL min^{-1} in all experiments. The column was placed in the column oven maintained at 160 °C. The SGIC separations were accomplished by applying a linear gradient from the adsorption promoting solvent to TCB (listed in the 'Materials and solvents' section). The volume fraction of TCB was increased linearly immediately after sample injection from 0% to 100% within 30 min (15 mL). The conditions were held for another 10 min before the initial chromatographic conditions were re-established with 100% adsorption promoting solvent. 200 μL of each sample was injected at a concentration of 1.2 mg mL^{-1}.

Results and discussion

Polypropylene stereoisomers

The separation of polypropylene (PP) according to tacticity or chemical composition on PGC has long been of interest since PP is of great industrial importance and it is used in everyday applications such as textiles, automotive and household appliances. Accordingly, better separation methods with improved selectivity, resolution and robustness of the chromatographic separation are of high interest. In the present study, the effects of the structure of the adsorption promoting component of the mobile phase and the column length (effect of the stationary phase) shall be studied.

In a first experiment, a blend of isotactic, syndiotactic and atactic polypropylene (iPP, sPP and aPP, respectively) in equal concentrations (1 : 1 : 1 ratio) was prepared. The molar masses of the PP stereoisomers are shown in Table 1. The three stereoisomers were soluble in all the adsorption promoting solvents investigated. TCB was used as desorption promoting solvent and a linear gradient from 0 to 100% TCB in 30 min was used. A column temperature of 160 °C was used throughout and Fig. 2a and b illustrate the elution behavior of the stereoisomers

Table 1 Molar masses and dispersities of the PP samples as obtained by HT-SEC-RI at 150 °C in TCB, molar masses are polystyrene equivalents

Sample	M_p [kg mol^{-1}]	M_w [kg mol^{-1}]	$Đ$
iPP	180.1	200.3	2.0
aPP	90.1	130.0	5.0
sPP	220.0	270.6	2.0

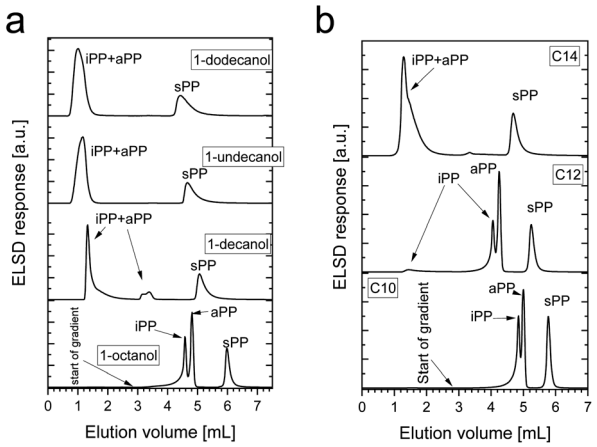

Fig. 2 Elution profiles of 1 : 1 : 1 blends of iPP, aPP and sPP in the alkyl alcohols 1-octanol, 1-decanol, 1-undecanol and 1-dodecanol (a) and in the alkanes decane, undecane and tetradecane (b). A 30 min gradient was applied from the adsorption promoting solvent to TCB and ELS detection was used.

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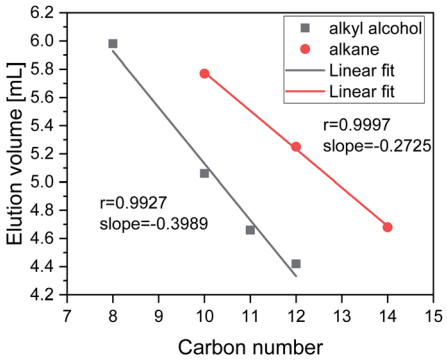

Fig. 3 Influence of alkyl alcohol and alkane chain length on the elution behaviour of sPP.

with different alkyl alcohols and alkanes as adsorption promoting solvents. All three stereoisomers are retained in 1-octanol and retention decreases with an increase in the alkyl chain length of the alcohol. This corresponds to a decrease in the polarity of the alcohols. iPP and aPP are partially retained in 1-decanol and not retained in solutions of the larger alcohols, *i.e.* 1-undecanol and 1-dodecanol.

On the other hand, the three stereoisomers are retained in decane (C10) and dodecane (C12). A small amount of iPP is not retained as illustrated in Fig. 2b. However, aPP and iPP are not retained in tetradecane and elute in the SEC mode *i.e.* before the start of the solvent gradient. In conclusion, when comparing alkanes and alcohols with similar alkyl chain lengths it is shown that the presence of the alcohol group does influence the retention behavior on PGC.

To evaluate the influence of the adsorption promoting solvent on the retention of sPP, the peak elution volume of the sPP fraction was plotted against the carbon number of the adsorption promoting solvent as illustrated in Fig. 3. Alkyl alcohols show a significantly steeper slope of −0.3989 as compared to −0.2725 for the alkanes. This implies that the change in elution behavior is more significant when the alkyl alcohol length size is changed. On the other hand, retention of aPP and iPP is lost when the alkyl chain length of the alkane/alcohol increases. This means that these components can be separated with 1-octanol, decane and dodecane but not with higher alkanes/alcohols.

A possible explanation for these observations is the increasing interaction between the adsorption promoting solvent and the stationary phase with increasing alkyl chain length of the adsorption promoting solvent. This applies to the alcohols as well as the alkanes. For the alcohols, however, this interaction is additionally affected by the polar hydroxyl groups.

This first experiment clearly indicates the significant influence of the adsorption promoting solvent on the separation of the PP isomers. In the following investigations, a more detailed study on this aspect shall be conducted.

Ethylene-*co*-1-octene copolymers

Polyethylene materials are widely used in many applications and can be easily tailor-made by varying their crystallinity. Linear low density polyethylene (LLDPE) is one such material with properties that can be significantly modified by changing the comonomer content. In the present work, a sample set of LLDPEs having 1-octene comonomer contents of 0.6–14.0 mol% (see Table 2) was utilized to investigate the effect of different chromatographic parameters on the chromatographic separation.

Table 2 Ethylene-*co*-1-octene copolymer samples, molar masses as determined by HT-SEC-RI are PS equivalents

Sample	1-Octene [mol%]	M_p [kg mol^{-1}]	M_w [kg mol^{-1}]	$Đ$
LLDPE 1	0.6	39.1	51.1	5.2
LLDPE 2	3.1	52.5	76.9	5.8
LLDPE 3	4.4	59.7	88.4	5.5
LLDPE 4	7.5	69.0	96.5	5.6
LLDPE 5	8.1	29.8	38.8	4.4
LLDPE 6	9.6	79.7	113.7	6.1
LLDPE 7[a]	10.0	73.1	98.4	5.5
LLDPE 8	10.2	46.6	65.7	5.3
LLDPE 9	11.1	96.4	132.1	5.6
LLDPE 10	14.0	103.3	136.8	5.0

[a] Not used for SGIC calibration.

Effect of the adsorption promoting solvent

As has been shown in the previous experiments, the adsorption promoting solvent may have a significant influence on the chromatographic behavior of polyolefins on PGC. This will be studied now for the solvent gradient systems alcohol → TCB and alkane → TCB where the alcohol/alkane is the adsorption promoting solvent while TCB is the desorption promoting solvent. The alkyl chain length of the alcohol/alkane is varied systematically to investigate the effect of solvent polarity on separation. With increasing alkyl chain lengths the solvent polarity is expected to decrease.

First, the samples were tested for solubility in the adsorption promoting solvents. All LLDPEs were soluble in these solvents, except for LLDPE 1–LLDPE 3 (0.6–4.4 mol% of 1-octene) which were not soluble in 1-octanol even after prolonged exposure to high temperature.

In a first set of experiments, the samples were injected onto a Hypercarb® PGC column with a length of 100 mm (4.6 mm i.d.) that is typically used for standard experiments. The solvent gradient method described in the Experimental section was used where a 30 min linear gradient was applied for good separation. The peak maximum elution volumes (V_e) obtained with the different adsorption promoting solvents were plotted as a function of the LLDPE comonomer content [C] as illustrated in Fig. 4a and b, resulting in linear functions with different slopes.

The retention behaviour for the alkyl alcohol → TCB solvent gradients clearly shows the influence of the alcohol chain length on the slopes being 1-octanol < 1-decanol < 1-undecanol < 1-dodecanol, see Fig. 4a. Therefore, as the length of the alkyl chain increases, the slope of the V_e *vs.* [C] plot increases, indicating better peak-to-peak separation. At low comonomer

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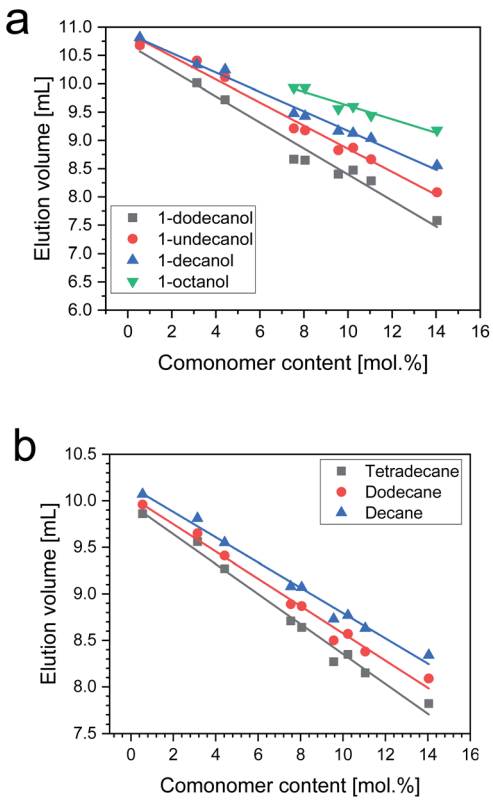

Fig. 4 Peak elution volume as a function of comonomer content with alkyl alcohols (a) and alkanes (b) as the adsorption promoting solvents.

Table 3 Peak elution volumes obtained from the gradient elution of LLDPEs with alkyl alcohols or alkanes as the adsorption promoting solvents, 30 min linear solvent gradient, 200 μL of 1.2 mg mL^{-1} sample solutions were injected

		Elution volume [mL]						
		Alkyl alcohol				Alkane		
LLDPE	1-Octene [mol%]	C8	C10	C11	C12	C10	C12	C14
1	0.6	—[a]	10.82	10.68	10.70	10.07	9.96	9.86
2	3.1	—[a]	10.34	10.41	10.02	9.81	9.65	9.56
3	4.4	—[a]	10.25	10.12	9.72	9.55	9.41	9.27
4	7.5	9.93	9.48	9.21	8.67	9.08	8.89	8.71
5	8.1	9.93	9.43	9.18	8.65	9.07	8.87	8.64
6	9.6	9.56	9.17	8.83	8.40	8.73	8.50	8.27
8	10.2	9.60	9.13	8.87	8.48	8.77	8.57	8.35
9	11.1	9.44	9.04	8.67	8.28	8.63	8.38	8.15
10	14.0	9.18	8.56	8.08	7.58	8.34	8.09	7.82

[a] Insoluble in 1-octanol.

contents *e.g.* at 0.6 mol%, the influence of the alkyl alcohol on elution volume is rather insignificant as clearly shown by the almost similar elution volumes for LLDPE 1 in Fig. 4a as well as Table 3. Differences in V_e are significantly more pronounced for LLDPE 10 in the different alcohols acting as adsorption promoting solvents.

Similarly, separation increases with increase in the length of the alkane for the alkane → TCB solvent gradient as illustrated by the increase in the slope *i.e.* decane < dodecane < tetradecane. Again, V_e of the low comonomer content LLDPE 1 is not significantly affected by the change in the alkane chain length as compared to LLDPE 10.

In the past, for polyolefin separations polarity has been discounted as an important attribute to the properties of adsorption promoting solvents.[16] From the present set of LLDPEs it is evident that the polarity of the adsorption promoting solvent influences separation. Fig. 5a and b compare the elution behavior of the LLDPEs when alcohols and alkanes with similar alkyl chain lengths are used. Here it is found that even when the carbon numbers are similar, the alcohol allows for a better separation of the LLDPEs. This indicates that the hydroxyl group of the alcohol plays an important role in the adsorption/desorption behavior on PGC.

The slope of the V_e *vs.* comonomer content plot gives an indication of the separation capability of the solvent gradient system. Since TCB was used as the sole desorption promoting solvent, it is easy to compare the slopes obtained with the different adsorption promoting solvents. The slope values were plotted as a function of the carbon number of the adsorption promoting solvent, see Fig. 5c. The change in the length of the alkyl chain results in better separation for the alcohols as well as the corresponding alkanes. It is clear, however, that this change is much more pronounced for the alcohols and, accordingly, better separations are obtained when alcohols are used as adsorption promoting solvents. The polarity of the adsorption promoting solvent, therefore, does play a role in the separation of the non-polar LLDPEs and PP.

Polarity and the alkyl chain length of the adsorption promoting solvent are two fundamental factors worth to be discussed more in detail. Solvent–solvent interactions which promote phase separation between solvent and polymer in solution might cause the observed differences between alkyl alcohols and alkanes. Particularly strong solvent–solvent interactions are expected for the alcohols that can interact *via* hydrogen bonds. The strength of the hydrogen bonds decreases with increasing alkyl chain length. On the other hand, solvent–polymer interactions must be considered to overcome polymer–polymer interactions to get the polymer molecules dissolved. Dissolution improves with increasing alkyl chain lengths as is seen in Table 3. Comparing now alcohols with alkanes it is obvious that any effects related to solvent–solvent and solvent–polymer interactions (including chromatographic resolution) will be more pronounced for alcohols due to the extra influence of the hydrogen bonding. This is confirmed by the steeper slopes for the alcohols as seen in Fig. 5c.

Effect of column length

Most of the work reported in literature for the separation of polyolefins utilises the 100 mm × 4.6 mm i.d. Hypercarb® column.[4,5,9,11,15,17,20,21] To investigate the effect of column length on the separation of LLDPEs, individual LLDPEs with comonomer contents of 0.6–14.0 mol% were injected into columns

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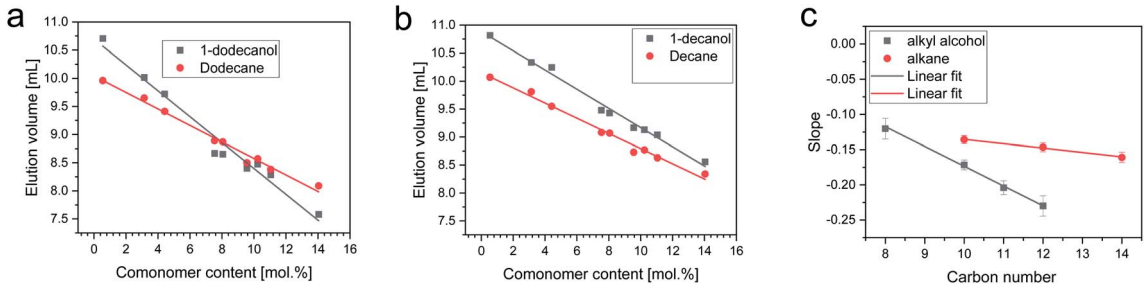

Fig. 5 Comparison of the elution behaviour of LLDPEs in 1-dodecanol and dodecane (a) as well as 1-decanol and decane (b). Slopes obtained from the gradient elution of LLDPEs with alkyl alcohols and alkanes as the adsorption promoting solvents as a function of the alkyl chain length (carbon number) (c).

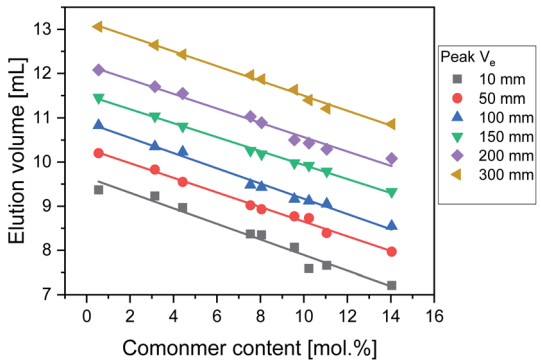

Fig. 6 Elution volumes of LLDPEs with 0.6–14.0 mol% 1-octene obtained at column lengths of 10–300 mm as a function of the comonomer content. A 1-decanol → $TCB_{30\ min}$ was used for all experiments at 0.5 mL min^{-1} mobile phase flow rate.

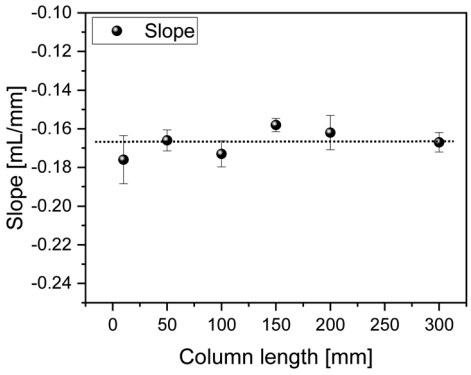

Fig. 7 Elution volume *vs.* comonomer content slope as a function of PGC column length.

with 10, 50, 100, 150 (combination of a 50 and a 100 mm column), 200 and 300 mm (combination of 2 × and 3 × 100 mm columns, respectively) lengths. V_e of the individual LLDPEs was plotted as a function of the comonomer content for each column length as illustrated in Fig. 6. The increase in V_e with increasing column length is attributed to an increase in the void volume. However, it is evident that the slopes of the V_e *vs.* comonomer plots do not significantly change with increasing column length. To better illustrate the steady nature of the slope/separation of the LLDPEs, the slopes of V_e *vs.* comonomer plots were presented as a function of the column length, see Fig. 7. Obviously, the increase in column length did not improve peak-to-peak separation.

To investigate the change in resolution as affected by the column length, 1 : 1 blends of LLDPE 1 (0.6 mol% 1-octene) and LLDPE 2 (3.1 mol% 1-octene) as well as LLDPE 4 (7.5 mol% 1-octene) and LLDPE 7 (10.0 mol% 1-octene) were made and injected onto the PGC columns using a 1-decanol → $TCB_{30\ min}$ solvent gradient. The elugrams obtained are shown in Fig. 8a and b. The blends were chosen based on the ^{13}C NMR average comonomer contents which are different by 2.5 mol% of 1-octene. It is evident from Fig. 8a that there is improvement in

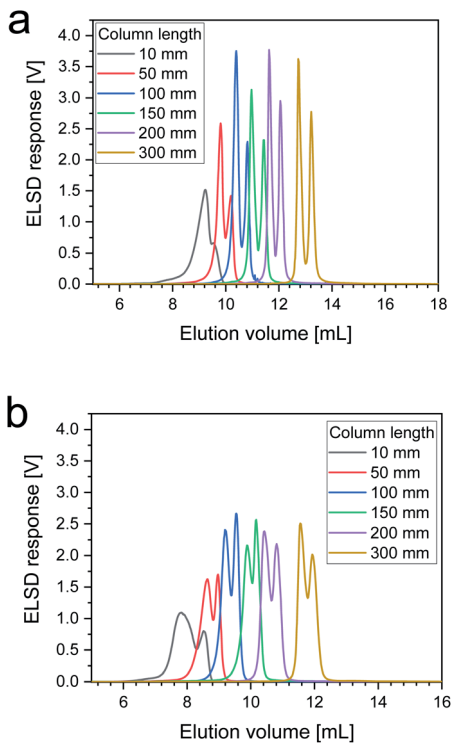

Fig. 8 Elution profiles of 1 : 1 blends of LLDPE 1 + LLDPE 2 (a) and LLDPE 4 + LLDPE 7 (b) obtained with a 1-decanol → $TCB_{30\ min}$ solvent gradient and column lengths of 10–300 mm. 200 μL of 1 mg mL^{-1} sample solutions were injected and the ELSD was used for detection.

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Table 4 Calculated resolution (R) from peak elution volume $V_{e\ max}$ and full width at half maximum (w) at column lengths of 10–300 mm for a 1 : 1 blend of LLDPE 1 and LLDPE 2

Column length [mm]	$V_{e\ max}$ [mL] LLDPE 1	LLDPE 2	$V_{e\ max\ (LLDPE\ 1)} - V_{e\ max\ (LLDPE\ 2)}$ [mL]	w [mL] LLDPE 1	LLDPE 2	R
10	9.24	9.55	0.31	0.42	0.83	0.29
50	9.80	10.20	0.40	0.20	0.42	0.76
100	10.40	10.81	0.41	0.22	0.19	1.20
150	10.97	11.42	0.45	0.22	0.19	1.30
200	11.63	12.05	0.42	0.17	0.16	1.49
300	12.73	13.22	0.49	0.20	0.18	1.53

Table 5 Calculated resolution (R) from peak elution volume $V_{e\ max}$ and full width at half maximum (w) at column lengths of 10–300 mm for a 1 : 1 blend of LLDPE 4 and LLDPE 7

Column length [mm]	$V_{e\ max}$ [mL] LLDPE 4	LLDPE 7	$V_{e\ max\ (LLDPE\ 4)} - V_{e\ max\ (LLDPE\ 7)}$ [mL]	w [mL] LLDPE 4	LLDPE 7	R
10	7.82	8.52	0.71	0.58	0.66	0.67
50	8.64	8.97	0.33	0.40	0.19	0.66
100	9.19	9.55	0.36	0.26	0.32	0.73
150	9.88	10.17	0.29	0.26	0.21	0.73
200	10.43	10.81	0.38	0.23	0.22	0.98
300	11.56	11.93	0.37	0.19	0.28	0.92

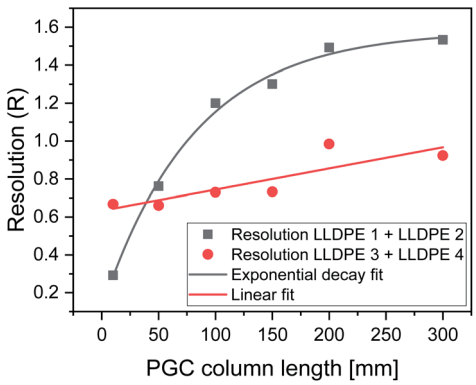

Fig. 9 Peak resolution as function of PGC column length for LLDPE 1 + 2 and LLDPE 4 + 7 blends.

chromatographic resolution for the low comonomer content LLDPEs 1 and 2 with increasing the column length from 10 mm to 300 mm. Although an increase in resolution is also observed for LLDPEs 4 and 7, this is not as pronounced as that of the low comonomer content LLDPEs.

Resolution of chromatographic peaks can be easily expressed in quantitative terms using eqn (1):[20]

$$R = \frac{2\left[V_{e\ max(x)} - V_{e\ max(y)}\right]}{1.7[w(x) + w(y)]} \quad (1)$$

where $V_{e\ max(x)}$ and $V_{e\ max(y)}$ correspond to the peak maximum elution volumes and $w(x)$ and $w(y)$ are the full width at half maximum (FWHM, w) of LLDPE x and LLDPE y, respectively.

The calculated resolutions (R) are reported in Tables 4 and 5 for the LLDPE 1 + 2 and LLDPE 4 + 7 blends, respectively. For better visualization, R is plotted as a function of the column length in Fig. 9. As can be seen, resolution increases significantly up to a column length of 150 mm for the LLDPE 1 + 2 blend. Although there is a visible increase in resolution after 150 mm, this is not as significant. Similarly, resolution of the LLDPE 4 + 7 blend increases, but not as significantly as that of the low comonomer blend.

The fact that the resolution of the LLDPE 1 + 2 blend is higher could be due to the influence of the comonomer content on band broadening *i.e.* different rates of migration through the column. For copolymers with higher comonomer contents a higher chemical composition heterogeneity is expected. As the peak broadness reflects the chemical composition heterogeneity, broader peaks are expected for copolymers with higher comonomer contents. On the other hand, at higher comonomer contents more chains have statistically more short chain branching arrangements (and, therefore, more complex diffusion patterns through the stationary phase) leading to broader elugrams which are difficult to resolve. This has been observed in several other studies involving ethylene-*co*-1-octene LLDPEs.[26,27]

From the data obtained in the preceding experiments, it was deduced that a 1-dodecanol → $TCB_{30\ min}$ solvent gradient gives better peak-to-peak separation while longer columns promote column efficiency and resolution. Therefore, a combination of the two conditions was applied to separate 1 : 1 blends of LLDPE 1 + LLDPE 2 and LLDPE 4 + LLDPE 7 as illustrated in

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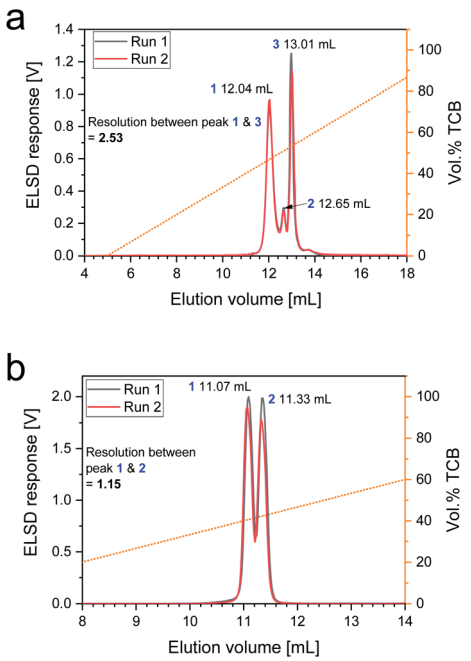

Fig. 10 Elugrams of 1 : 1 blends of LLDPE 1 + LLDPE 2 (a) and LLDPE 4 + LLDPE 7 (b) obtained at a 1-dodecanol → $TCB_{30\ min}$ solvent gradient and ELSD detection. 200 μL of 1.2 mg mL^{-1} polymer solutions were injected and the ELSD was used for detection.

Fig. 10a and b. Similar gradient and temperature conditions as in the preceding experiments were used *i.e.* 1-dodecanol → $TCB_{30\ min}$ at 160 °C and a mobile phase flow of 0.5 mL min^{-1}. It is evident from the elugrams that significantly better separation and resolution can be achieved for the LLDPE 1 + 2 in Fig. 10a and LLDPE 4 + 7 in Fig. 10b in comparison to the 1-decanol → $TCB_{30\ min}$ gradient in combination with a 100 mm column, compare to Fig. 8. In addition to the separation of the two main components of LLDPE 1 + 2 a third component becomes visible between the two main peaks. This component is due to additionally resolved material from both LLDPE 1 and LLDPE 2. Similarly, an improvement in the peak resolution was observed for LLDPE 4 + 7. However, the peak resolution between the two copolymers is not as significant as that of the low comonomer content counterparts. This may lead to the speculation that the comonomer content plays a role in peak resolution as was discussed before. However, the inherent chemical composition distribution of the blend components can also influence the resolution although this is not expected to be the case in the present study. As a higher volume (200 μL) was intentionally injected onto the PGC column, better resolution can still be obtained by lowering the injection volume to the usual 20–50 μL.

Conclusions

In this study, the effects of the adsorption promoting component of the mobile phase and the column length (volume of the stationary phase) on the separation behaviour of polyolefins in solvent gradient interaction chromatography were investigated. It was shown that linear primary alkyl alcohols yield better separation of polypropylene (PP) and linear low density polyethylene (LLDPE) as compared to linear alkanes when used as adsorption promoting solvents. The separation increased in the order 1-octanol < 1-decanol < 1-undecanol < 1-dodecanol. Although an increase in separation was also observed with the linear alkanes decane, dodecane and dodecane in that order, the improvements in separation were not as pronounced. Increasing the column length from 10 mm to 300 mm was shown to improve column efficiency for the separation of LLDPEs particularly for copolymers with low comonomer contents. A 1-dodecanol → TCB solvent gradient in combination with a 300 mm column was used to produce the highest resolution of binary LLDPE blends. The fact that the degree of improvement for copolymers with higher comonomer contents was lower has been attributed to the increase in statistical intra- and interchain comonomer/short chain branching variations with increasing LLDPE comonomer contents which consequently gives rise to broader elution profiles which are more difficult to resolve.

Conflicts of interest

There are no conflicts of interest to declare.

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