

Elution behavior of polyethylene in polar mobile phases on a non-polar sorbent

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Abstract

Linear polyethylene standards in the range of 1–500 kg/mol, dissolved in 1,2,4-trichlorobenzene, were injected into a column packed with oligo(dimethylsiloxane) modified silica gel. Fifteen polar solvents (cyclohexanone, cyclohexylacetate, cyclohexanol, nonylalcohol, dimethylformamide, dimethyl sulfoxide, ethylene- and diethylene glycol monobutyl ether, benzylalcohol, hexylacetate, bis(2-ethyl-hexyl)phthalate, *N,N*-dimethylacetamide, propylene carbonate, dipropylene glycol and *N*-methyl-pyrrolidone) were evaluated as mobile phases. Depending on the type of mobile phase evaluated, different elution behaviors are observed for polyethylene: (1) polyethylene was eluted in the size exclusion mode, (2) polyethylene was eluted together with the sample solvent peak at constant elution volume, (3) polyethylene was partially or fully retained on the column. The retained polymer was easily removed from the column by injecting a small volume of trichlorobenzene. The use of ethylene glycol monobutyl ether as the mobile phase enabled separation of the polyethylene from polypropylene. In this case polypropylene is eluted in the size exclusion mode, while polyethylene is eluted at a constant elution volume or remains in the column.

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1. Introduction

Polyethylene (PE) is commercially one of the most important polymers [1]. It exhibits very good mechanical properties, which are mainly due to its semicrystalline structure, and excellent chemical resistance. From the analytical point of view, these

properties are responsible for difficulties in the analytical characterization of polyethylene-based materials. The molecular characterization of polymers usually requires the dissolution in a solvent. PE is not soluble in any solvent at room temperature and the destruction of the crystalline domains requires specific solvents, dissolution temperatures of 130–160 °C and extended dissolution times. At present, 1,2,4-trichlorobenzene or 1,2-dichlorobenzene are commonly used as solvents for PE [2]. However, it is known that more polar solvents can dissolve PE [3]. Table 1 summarizes solvents and theta solvents for linear polyethylene, published in the literature.

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Table 1
Solvents for polyethylene and corresponding theta temperature

Solvent	Theta temperature (°C)	Ref.
Aliphatic, cycloaliphatic and aromatic hydrocarbons, halogenated aliphatic, cycloaliphatic and aromatic hydrocarbons, higher aliphatic esters and ketones, di- <i>n</i> -amyl ether		[3]
<i>n</i> -Pentane	~85	[4]
<i>n</i> -Hexane	133	[4]
<i>n</i> -Heptane	173.9	[4]
<i>n</i> -Octane	210	[4]
Biphenyl	125	[5]
Diphenylmethane	142.2	[6]
<i>p</i> - <i>tert</i> -Amyl alcohol	199.2	[6]
<i>n</i> -Octanol	180.1	[6]
<i>n</i> -Decanol	153.3	[6]
<i>n</i> -Dodecanol	137.3	[6]
<i>p</i> -Octyl phenol	174.5	[6]
<i>p</i> -Nonyl phenol	162.4	[6]
Diphenyl ether	161.4	[7]
Benzyl phenyl ether	191.5	[6]
Diphenylene oxide	~118	[5]
Methoxybenzene	153.3	[6]
Nitrobenzene	>200	[5]
3,5,5-Trimethyl-hexylacetate	126	[8]
Bis(2-ethylhexyl) adipate	145	[9]
Bis(2-ethylhexyl) sebacate	150	[5]
Dibutyl phthalate	>200	[5]

Mixtures of solvents and non-solvents are frequently used for preparative fractionation of PE by stepwise precipitation [10]. Stepwise precipitation explores the dependence of the solubility at a specific temperature on molar mass, composition and architecture [10]. This separation method is, however, labour intensive and time consuming. Moreover, selectivity towards small differences in molar mass or chemical composition is rather low. The dependence of the solubility of PE on temperature is used for separating PE by temperature rising elution fractionation (TREF) [11] and CRYSTAF [12]. Both methods explore the crystallization of PE in temperature gradients and are well established methods for the characterization of short chain branching of linear low density polyethylene.

Out of the variety of liquid chromatographic techniques, only high-temperature size-exclusion

chromatography (HT-SEC) is used for PE materials [13]. While various methods of adsorption chromatography [14,15] are available for amorphous and commercially significant polymers such as polystyrene (PS), polymethylmethacrylate (PMMA), polybutadiene, etc., this is not the case for PE. Limited solubility of PE and inertness of PE macromolecules against known sorbents are possible reasons for this. Moreover, liquid chromatography measurements with PE require special experimental setups operating at 130–150 °C, which are not readily available.

In recent years, following the discovery of metallocene catalysts, a large number of functionalized PE homopolymers as well as copolymers were synthesized [16–18]. For these products, in addition to the molar mass distribution, the distribution in chemical composition is of interest for research purposes. This is the reason why new analytical separation systems are needed for PE.

In literature, there are no data on the interactive liquid chromatography of PE. PE chains are non-polar and should adsorb on non-polar sorbents from polar liquids. The most common hydrophobic chromatographic sorbents are based on silica gel, which are chemically modified with alkyl groups. It is known that these sorbents contain various concentrations of free silanol groups, i.e. their surface is not homogeneously non-polar. The presence of free silanol groups influences the retention behavior of small molecules significantly. Recently, Berek has demonstrated very different interactivities of commercially available silica gel C₁₈ sorbents with regard to the elution behavior of polymeric solutes [19]. Depending on the column manufacturer, polymethylmethacrylates in toluene were either eluted in the SEC mode, eluted at a constant elution volume, or were fully retained within the silica gel C₁₈ column packing. Large differences in interactivity were also found in the case of polystyrene/divinylbenzene columns from various producers, when tested with polymeric solutes [20].

The presence of polar groups on silica-based reversed-phase sorbents is possibly one of the reasons why alkanes are adsorbed on these sorbents only from very polar mobile phases, such as methanol/water [21]. Such polar liquids are however, non-solvents for large PE chains.

In gas chromatography, dimethylsiloxane columns are used for the separation of alkanes. Separation of alkanes in these columns is very selective [22]. A new highly hydrophobic sorbent based on silica gel with a surface coverage of oligo(dimethylsiloxane) was recently described [23,24]. On the surface of this sorbent all silanol groups are fully blocked by bulky dimethylsiloxane chains. Further, carbon in poly(dimethylsiloxane) is present only in the form of methyl groups (CH_3), which have lower surface energy (more lyophobic) than methylene groups (CH_2), the major part of *n*-alkyl chains. Moreover, this covalently bonded layer of oligo(dimethylsiloxane) on silica gel is stable up to 350–380 °C [23]. In this paper, we describe the elution behaviour of PE in polar mobile phases on a stationary phase of silica gel chemically modified with oligo(dimethylsiloxane).

2. Experimental

For all measurements, a Waters 150C chromatograph (Waters, Milford, USA) was used, connected to an evaporative light scattering detector (ELSD, model PL-ELS 1000, Polymer Laboratories, Shropshire, UK). ELSD has the advantage that the mobile phase is evaporated. Therefore, peaks of solvents are not detectable and only the polymer is detected. The following ELSD parameters were employed: gas flow-rate 0.5 l/min, nebulization temperature 200 °C, evaporation temperature 270 °C. Both the column oven and the polymer samples in the autosampler were maintained at 140 °C. The mobile phase was preheated to 140 °C in the injector compartment; 25 μl of polymer dissolved in 1,2,4-trichlorobenzene with a concentration of around 1 mg/ml was injected into the column. Antioxidant was not added to the sample solution because the antioxidant (Irganox 1010) was detected as a high peak on the chromatogram. It was supposed that extent of polymer degradation through the measurement is small and it may be neglected. Flow-rate of the mobile phase was 0.4 ml/min.

2.1. Sorbent and column

The sorbent was prepared via reaction of hydrated

silica gel with dimethyldichlorosilane as described in Ref. [23]. According to a previous investigation [23], the major products of this reaction are oligo(dimethylsiloxane) loops, covalently attached to silica by two Si–O–Si bonds (see reaction scheme in Fig. 1). The grafting density of the dimethylsiloxane repeat units $[(\text{CH}_3)_2\text{SiO}]$ was ~ 6.4 group/ nm^2 as determined from carbon analysis.

Pure, unmodified silica gel supplied by Jupiter (Phenomenex, Torrance, CA, USA) has an average pore size of 340 Å, a surface area of 170 m^2/g , a pore volume of 1.51 ml/g and a particle diameter of 5 μm . The sorbent was packed into a 100×4.6 mm I.D. column.

2.2. Solvents

1,2,4-Trichlorobenzene (TCB), cyclohexanone, cyclohexanol, cyclohexylacetate, ethylene glycol monobutyl ether (EGMBE), nonylalcohol, dimethyl sulfoxide (DMSO), benzylalcohol, hexylacetate, bis(2-ethyl-hexyl)phthalate, dipropylene glycol and *N*-methyl-pyrrolidone (NMP) were obtained from Merck (Darmstadt, Germany). These solvents were of synthesis grade quality. Dimethylformamide (DMF) and diethylene glycol monobutyl ether (DEGMBE), both for synthesis, were products of Acros Organics (New Jersey, USA). *N,N*-Dimethylacetamide (HPLC quality) was delivered by Fluka (Buchs, Switzerland).

2.3. Polymers

Linear polyethylene (PE) standards with average molar masses between 0.74 and 145 kg/mol were

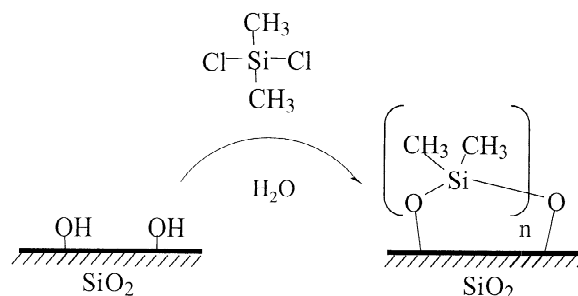


Fig. 1. Reaction scheme for the chemical modification of the silica surface.

supplied by Polymer Standard Service (Mainz, Germany). Their polydispersity (M_w/M_n) was in the range of 1.2–1.7. PE with weight average molar masses of 260 kg/mol, 500 kg/mol and polypropylenes (PP) with weight average molar masses of 200 kg/mol, 438 kg/mol were acquired from PCD (Linz, Austria). Their polydispersity M_w/M_n was in the range of 3–6. PP 36 kg/mol and 57 kg/mol (M_w/M_n 2.5 and 2.1) were obtained from the Dept. of Chemistry, University of Stellenbosch and characterized at the German Institute for Polymers, Darmstadt.

3. Results and discussion

PE standards were dissolved in TCB at 140 °C and injected into the column packed with the oligo(dimethylsiloxane) sorbent. The elution was conducted with a series of single mobile phases of different polarity and the elution behavior of PE is illustrated in Fig. 2.

With polar solvents that readily dissolve PE (cyclohexanone, nonylalcohol, hexylacetate, cyclohexylacetate, cyclohexanol), PE is eluted in the SEC mode at high recoveries. The chromatographic behavior of the PE samples in cyclohexanol is shown in Fig. 3. Similar chromatograms are obtained with nonylalcohol and cyclohexanone as mobile phases. A smaller peak tailing compared to cyclohexanol was observed in cyclohexylacetate, hexylacetate and TCB. Injection of PE standards after dissolution in cyclohexanone or hexylacetate leads to the the same size exclusion elution behavior.

As the PE standards were injected in 1,2,4-trichlorobenzene as the solvent, large solvent peaks appear in the chromatograms using refractive index detection. These solvent peaks are not detected with the ELSD.

For mobile phases that are non-solvents for PE, the elution can be described in the following way: PE macromolecules move through the column faster than the small molecules of TCB. When the macromolecules leave the TCB-peak and the mobile phase is a non-solvent, PE is precipitated. When the TCB-peak reaches the precipitated PE, PE is redissolved in the TCB peak (of course, only when PE is soluble at the given composition of TCB/polar liquid in the

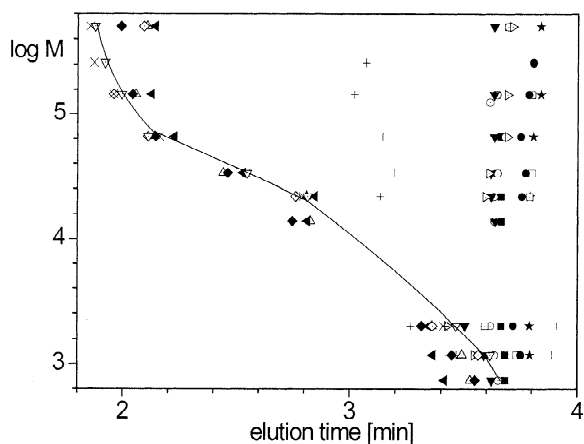


Fig. 2. Elution behavior of polyethylene standards in single polar mobile phases. Sample solvent: TCB. Column packing: Silica gel with covalently bonded oligo(dimethylsiloxane). Temperature: 140 °C. Symbols: TCB (inverted open triangle); nonylalcohol (upright open triangle); cyclohexanone (filled lozenge); cyclohexanol (left facing filled triangle); cyclohexylacetate (diagonal cross); hexylacetate (open lozenge), benzylalcohol (filled square); DEGMBE (inverted filled triangle); EGMBE (right facing open triangle); DMSO (filled star); DMF (open circle); *N,N*-dimethylacetamide (open square with centred dot); bis(2-ethylhexyl)phthalate (upright cross); NMP (filled circle); dipropylene glycol (horizontal dash); propylene carbonate (vertical line); SEC calibration curve for polyethylene in TCB (solid line).

TCB-peak). As a result, PE with different molar masses elute together with the TCB-peak, i.e. at constant elution volume (Figs. 4 and 5). This elution

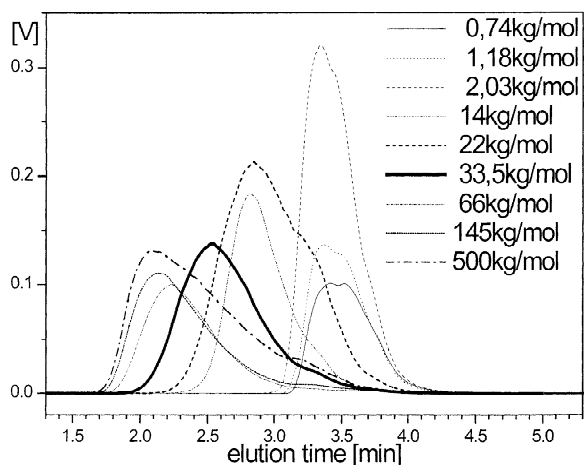


Fig. 3. Chromatograms of PE standards injected in TCB. Mobile phase: cyclohexanol. Temperature: 140 °C.

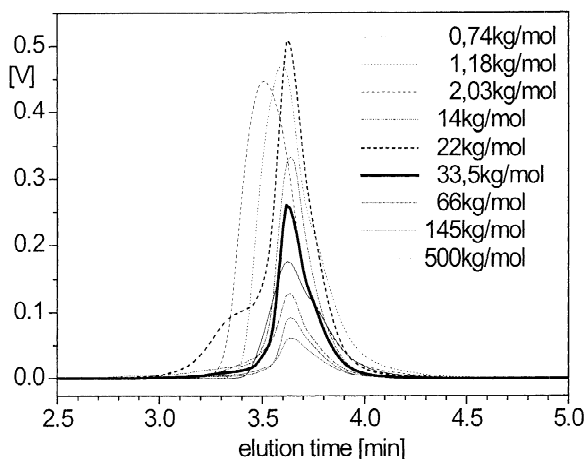


Fig. 4. Chromatograms of PE standards injected in TCB. Eluent: DEGMBE. (Note: PE 1.18 kg/mol; 2.03 kg/mol and PE 22 kg/mol partially elute in SEC mode.) Temperature: 140 °C.

mechanism is known as liquid chromatography under limiting conditions [25–27]. For polyethylene this phenomenon has not been described yet.

Using DEGMBE and comparing the peak heights in Figs. 4 and 5, it seems that almost all PE standards are eluted from the column. On the other hand, in DMF (Fig. 5), only PE with molar masses less than 2 kg/mol are eluted. DEGMBE and DMF are non-solvents for PE, therefore PE is eluted under limiting conditions of solubility.

In mono- and diethylene glycol monobutyl ether

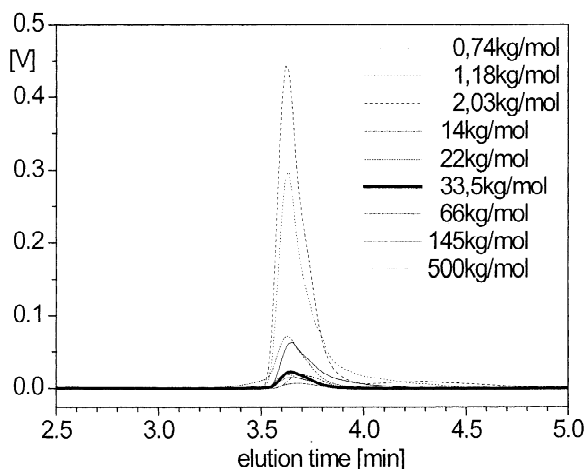


Fig. 5. Peaks of PE standards injected in TCB. Mobile phase: DMF. Temperature: 140 °C.

(EGMBE, DEGMBE) and benzylalcohol, PE in a broad range of molar masses is eluted under limiting conditions in the solvent (TCB) peak, almost independently of molar mass. Recovery of PE however, decreases with increase in the molar mass.

Very limited recovery of PE was found using DMSO and DMF (Fig. 5) as mobile phases. It appears that PE with molar masses lower than about 2 kg/mol are soluble in the majority of the tested liquids. The PE standards used have rather broad molar mass distributions, i.e. the standards may contain chains with molar masses as small as 1–2 kg/mol. As a result, after injection of a PE standard, a peak of polymer appears in the chromatogram even in the case where the polymer is almost fully retained in the column. Retained PE are easily removed from the column by injection of 200 μ l of TCB (1–3 injections).

When NMP and *N,N*-dimethylacetamide are used as mobile phases, peak splitting has been observed, i.e. the polymer elutes in two peaks, the first in the SEC mode, and the second together with the solvent peak (Fig. 6). The first peak contains macromolecules, which are soluble in the mobile phase. A small tendency towards peak splitting is also found using DMSO as the mobile phase.

It is known that peak splitting occurs in some liquid chromatographic systems if the sample solvent and the mobile phase differ in composition [28]. In

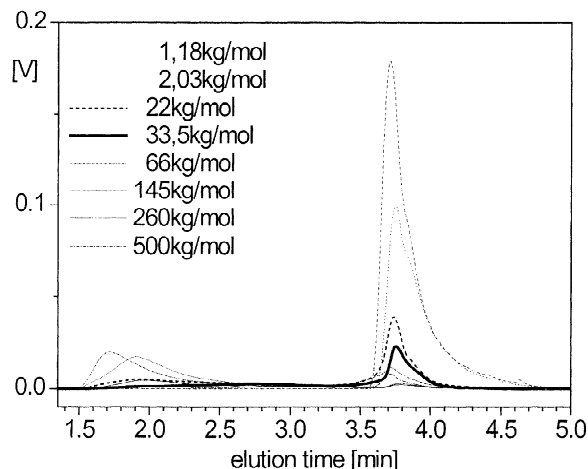


Fig. 6. Peak splitting for PE standards injected in TCB. Mobile phase: NMP. Temperature: 140 °C.

our case, the extent of this phenomenon is quite limited, because a large part of the polymer is retained within the column and is flushed out only by injection of larger volumes of TCB.

In mobile phases *N,N*-dimethylacetamide and NMP peak splitting is observed, while in *N,N*-dimethylacetamide and DMSO it is not observed. In the case of the peak splitting, the peak with the smaller elution volume contains macromolecules which are soluble in the mobile phase. It means that *N,N*-dimethylacetamide and NMP should be less polar and thus better compatible with PE, than DMF and DMSO. According to our cloud point measurements at 140 °C (unpublished research), PE 260 kg/mol is soluble above 55% vol. NMP or *N,N*-dimethylacetamide and up to 48% DMF and 20% DMSO in mixtures TCB plus the corresponding non-solvent. This means that the extent of the polymer solubility in the mobile phase determines the elution behavior of PE.

When dipropylene glycol and propylene carbonate were used as mobile phases, almost all injected polymer molecules were retained within the column. Small polymer peaks were however, still observed in the chromatograms.

It is known that EGMBE is a solvent for PP at 164 °C and even PP with molar masses of 800 kg/mol are soluble at this temperature, while EGMBE is non-solvent for PE [29]. As a result, PP elutes in EGMBE in the SEC mode, while PE elutes under limiting conditions (Fig. 7), i.e. in the solvent peak plus a part of PE that is precipitated in the column.

This system is suitable for the separation of PE–PP polymer blends, as illustrated in Fig. 8. Polystyrene, polybutadiene, polymethylmethacrylate and polyvinylchloride may also be separated from PE in this mobile phase, because they elute with EGMBE in the SEC mode. The retained amount of PE may be removed from the column by injection of 200 μ l TCB. It is important to note that for the present HPLC measurement a temperature of 140 °C was used, limiting the solubility of PP in EGMBE to about 60–100 kg/mol. PP with higher molar masses are precipitated at 140 °C. A temperature of about 165 °C would be necessary for full elution of high molar masses of PP.

For comparison, we injected PE in TCB into a

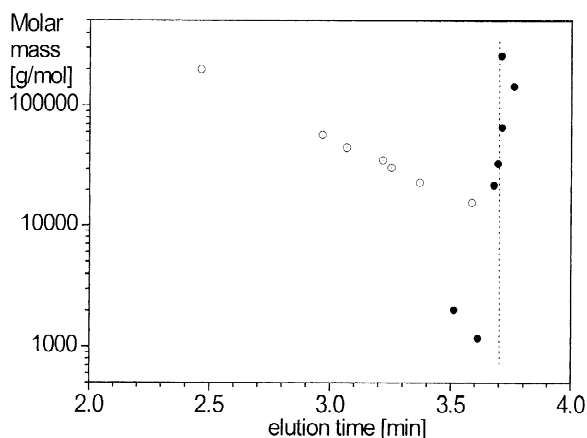


Fig. 7. Elution behavior of PE and PP injected in TCB. Mobile phase: EGMBE. Temperature: 140 °C. Symbols: ●, PE standards; ○, PP standards.

Nucleosil C₁₈ column with DEGMBE as the mobile phase. A much larger amount of polymer was fully retained on this stationary phase compared to the silica gel with oligo(dimethylsiloxane). This may be caused by preferential solvation of the sorbent by solvent molecules. It is known that silica gel C₁₈ contains residual free hydroxyl groups that may adsorb polar molecules from the mobile phase

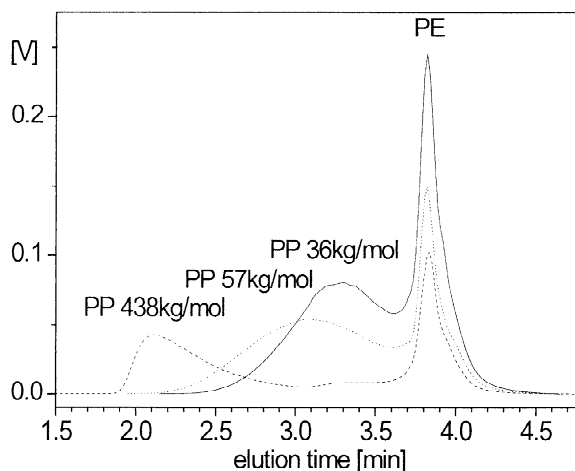


Fig. 8. Separation of polymer mixtures. PE and PP injected in TCB. Mobile phase: EGMBE. Temperature: 140 °C. Symbols: solid line, blend PP 36 kg/mol with PE 34 kg/mol; dotted line, blend PP 57 kg/mol with PE 66 kg/mol; dashed line, blend PP 438 kg/mol with PE 500 kg/mol.

(impurities, such as water in DEGMBE or others) and these may cause a precipitation of PE.

4. Conclusion

The investigation of the elution behaviour of polyethylene on a non-polar stationary phase has shown:

1. Polyethylenes up to 500 kg/mol are eluted in the SEC mode when the mobile phase is a solvent for PE, such as cyclohexanone, cyclohexanol, cyclohexylacetate, hexylacetate, nonylalcohol (i.e. molecules with one large non-polar part and one small polar part). This enables HPLC characterization of some PE-PMMA and PE-PS copolymers (unpublished research). Cyclohexanol was never mentioned as a solvent for PE before, however, PE 145 kg/mol is soluble in cyclohexanol at 140 °C.
2. Polyethylene is eluted under limiting conditions when the mobile phase is a non-solvent for PE, such as benzylalcohol, EGMBE, DEGMBE (i.e. molecules with two or more polar parts), however, with limited polymer recovery. As has been shown, polyethylene may be selectively separated from polypropylene in single mobile phase ethylene glycol monobutyl ether. EGMBE is a solvent for PP and a non-solvent for PE.
3. Polyethylene is largely retained, if not precipitated, when the mobile phase is a very polar liquid and a non-solvent for PE, such as dimethylformamide, dimethyl sulfoxide (i.e. small and very polar molecules). In dipropylene glycol and propylene carbonate, PE is most strongly retained. Retained PE can be eluted from the column with a small volume of TCB (200 μ l 1–3 \times injected). This is an indication that a gradient elution from non-solvent to solvent could be feasible.
4. Silica gel covered with a covalently bonded layer of oligo(dimethylsiloxane) is stable under conditions of high-temperature HPLC. No change in retention or in column efficiency of the column used was observed after a few months in the column oven.

To our knowledge, this is the first paper dealing with the elution behavior of polyethylene from polar liquids. As has been shown, polyethylene may be

eluted in polar liquids in the SEC mode up to high molar masses or can be retained on the stationary phase in various extents. The different elution behavior of PE and PP enables their separation even using a single mobile phase. Suitable combinations of liquids with different polarities should enable retention adjustment of PE and thus the exploitation of interactive HPLC in the analytical characterization of polyolefins.

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