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# Liquid Chromatographic Separation of Olefin Oligomers and its Relation to Separation of Polyolefins – an Overview

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**Summary:** Linear and branched alkanes are oligomers of polyethylene. Alkanes with higher molar masses are called waxes. These substances are widely used as fuels, oils, lubricants, etc. and for these reasons many groups have tried to analyse, separate and characterise alkanes by various methods, including liquid chromatography. Alkanes may be separated according to their size in solution by SEC. In addition to chromatographic systems separating in the SEC mode, various sorbent-solvent systems have been published, where alkanes have been separated one from another by adsorption and/or precipitation mechanism. The mobile phase is either a non-polar solvent or a polar solvent or a mixture of a solvent and a non-solvent for alkanes. Even near critical conditions, which have several advantages for applications of HPLC in polymer analysis, have been identified for alkanes. Moreover, selective separations of branched alkanes according to their structure have been published. In the majority of these published studies, solvents with low boiling points have been used as the mobile phases, which do not allow dissolution of crystalline polyolefins at atmospheric pressure. However, taking into account experiences with the separation of alkanes, new HPLC systems for the separation of polyolefins may be developed. This is a major challenge and first results are presented in this contribution.

**Keywords:** alkanes; liquid chromatography; polyolefins

## Introduction

Linear and branched alkanes are oligomers of polyethylene which belongs to the class of polyolefins. Alkanes with higher molar masses are called waxes. These materials are very useful in every day life and for this reason many groups have tried to analyse, separate and characterise these materials by various methods, including liquid chromatography. In the following paragraphs typical as well as unusual separation results published in the literature will be reviewed.

## SEC Mode of Alkanes

SEC-like separations of linear and branched alkanes have been observed in various column packing – mobile phase pairs (Table 1). The elution volumes of alkanes decreased with increasing molar masses, however, there were, depending on the solvent used, substantial differences in the dependence of the elution volume on the molar mass of the alkanes, probably due to small differences in enthalpic interactions of the alkanes with the column packings. In majority of cases namely the polar mobile phases have been used, where only alkanes with small number of carbons in molecules are soluble.

Due to problems with solubility of alkanes with a higher carbon numbers at ambient temperature, SEC of alkanes and waxes is often realized under the same

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***Table 1.***
SEC mode of alkanes.

| Number of carbon atoms in alkane | Column | Mobile phase* | Temperature [°C] | Reference |
|---|---|---|---|---|
| 5–16 n-alkanes | Styragel | toluene, THF, benzene, o-dichlorobenzene, chlorobenzene | 25 | [1] |
| 5–16 n-alkanes | Styragel | THF, toluene, benzene, chlorobenzene, o-dichlorobenzene, butyl acetate, ethyl acetate, 1,2-dichloroethane | 25 | [2] |
| 7–28 n-alkanes, cycloalkanes | Sephadex LH-20 | petroleum ether | ambient | [3] |
| 18–30 n-alkanes | Styragel | THF | 30 | [4] |
| 20–160 n-alkanes | silica gel | toluene | 40 | [5] |
| 16–48 n-alkanes | Styragel | ODCB, toluene, THF | 80 (toluene, ODCB) 30 (THF) | [6] |
| 5–16 n-alkanes | Merkogel (polyvinyl-acetate gel) | chloroform, benzene, toluene, p-dioxane, THF, acetone, ethyl acetate, Me, n-butyl acetate, methyl- ethylketone | 25 | [7] |
| 6–30 linear and branched alkanes | TSK G2000 H8 | THF | ambient | [8] |
| 6–28 n-alkanes | porous glass, PS/DVB | THF | 23 | [9] |
| 5–12 alkanes and branched alkanes | PS/DVB | THF | ambient | [10] |
| 5–16 n-alkanes | silica gel C18* | n-hexane, decane, n-tetradecane, n-heptadecane | 25 | [11] |
| 7–11 branched alkanes | Styragel | THF | 23 | [12] |
| 6–20 1-alkenes, cycloalkanes | Spheron P-300 (copolymer of 2-hydroxyethyl methacrylate/ ethylene dimethacrylate) | n-heptane | ambient | [13] |
| C5–C50 n-alkanes | Jordi columns DVB | TCB | 145 | [14] |

*Symbols: THF – Tetrahydrofuran, TCB – 1,2,4-trichlorobenzene, ODCB – o-dichlorobenzene, Me – methanol., ACN – acetonitrile, silica gel C18 – silica gel with chemically bonded octadecyl chains.

high-temperature conditions as SEC of polyolefins. We suppose that PS/DVB and silica gel in combination with the mobile phase such as TCB, ODCB or toluene are the most suitable for SEC of alkanes. Gas chromatography offers, however, much better separation of alkanes (i.e., one base line separated peak for each alkane) until carbon number C50.[15]

## Interactive Liquid Chromatography of Alkanes

Many groups have measured the retention of alkanes on sorbents in various liquids (Table 2 and 3). The alkanes have been dissolved usually in a single solvent and separated most often at room temperature. As a rule, the retention volumes increased with the molar mass of the alkanes (Figure 1). The molar masses of the alkanes were, however, limited due to insolubility of alkanes with higher carbon numbers in the tested liquids.

In polar liquids, there is a markedly increased preference of hydrocarbon solutes for the less polar stationary phase. The retention of an alkane is larger on silica gel with bonded $C_{18}$–chains than on bonded $C_3$-chains (Table 3, [32,36]). Increasing the polarity of the eluent leads to increased retention of the alkanes (Table 2, [18], Table 3, [32]). On the other hand, using nonpolar solvents, such as perfluoroalkanes, alkanes are adsorbed on typical polar sorbents, such as silica gel (Table 2,[20–23]). An increase of the temperature decreased the retention of alkanes in all tested systems (Table 2,[17,19,29]).

***Table 2.***
HPLC of alkanes in single mobile phases.

| Number of carbon atoms in alkane | Column | Mobile phase | Temperature [°C] | Reference |
|---|---|---|---|---|
| 9–16 n-alkanes | Styragel | acetone | 25 | [2] |
| 5–20 n-alkanes | silica gel C18 | Me, ethanol, isopropanol, ACN | ambient | [16] |
| 6–17 | silica gel C18 | Me | −15–+55 | [17] |
| 9–32 n-alkanes | silica gel C18 | Me, ethanol, propanol, butanol | 23 | [18] |
| 6–22 n-alkanes | silica gel C18 | Me | 25–60 | [19] |
| 5–20 n-alkanes | silica gel alumina | perfluorocyclic ether, n-pentane | 23 | [20] |
| 5–12, 1-alkenes, alkyldiene | silica gel | perfluoroalkane | ambient | [21] |
| 6–18, n-alkanes, 1-alkenes, alkyldiene | silica gel | perfluoroalkane, heptane/perfluoroalkane | 20 | [22] |
| 6–16 n-alkanes | silica gel | isooctane/perfluoro-alkane | ambient | [23] |
| 5–12 n-alkanes, cyclo-alkanes | silica gel C18 | Me | 23 | [24] |
| 5–10 n-alkanes | silica gel C18 | Me | 23 | [25] |
| 7-16 linear and branched alkanes | zeolite ZSM-5, zeolite ZSM-5, zeolite silicalite | n-hexane, n-octane, Me | ambient | [26] |
| 5–16 n-alkanes, 1-alkenes | silica gel silica gel (modified with a copper salt) silica gel (modified with a silver salt) | n-pentane, perfluoroalkane | ambient | [27] |
| 5–14 n-alkanes | copoly(isodecylmethacrylate-divinylbenzene) | Me, ethanol, cyclohexane | | [28] |
| 8–22 n-alkanes | silica gel C18 | Me | −32–+35 | [29] |
| 6–10 n-alkanes | alkylvinylether copolymers (alkyl = C4 and C18) | Me | 20 | [30] |
| 6–15 n-alkanes, branched alkanes, cyclo-alkanes | carbon | Me | 24 | [31] |

An especially strong retention of alkanes as well as the influence of topology of alkanes on this retention have been observed on zeolites (Table 2). Adsorption of alkanes on several organic sorbents, including Styragel, a typical column packing for SEC of polyolefins, has been also described (Table 2,[2]). Experimental conditions for retention of polyolefins on organic sorbents, however, have not been identified.

***Table 3.***
HPLC of alkanes in mixed mobile phases.

| Number of carbon atoms in alkane | Column | Mobile phase | Temperature [°C] | Reference |
|---|---|---|---|---|
| 5–20 n-alkanes | silica gel C18 | dioxane/water THF/water | ambient | [16] |
| 2–32 n-alkanes | silica gel C1, silica gel C8, silica gel C14, silica gel C18 | Me/water Me/THF | 25 | [32] |
| 5–11 linear and branched alkanes | silica gel 18 | Me/water | 20 | [33] |
| 20–44 n-alkanes | silica gel C18 | THF/water | 50 | [34] |
| 5–14 n-alkanes | vinyl alcohol copolymer grafted with C18 chains, silica gel-C18 | Me/water | ambient | [35] |
| 5–10 n-alkanes | silica gel C3, silica gel C8, silica gel C18 vinyl alcohol copolymer grafted with C18 chains | ACN/water | 30 | [36] |
| 5–14 n-alkanes | silica gel C18 | ACN/chloroform, Me/chloroform | 20 | [37] |

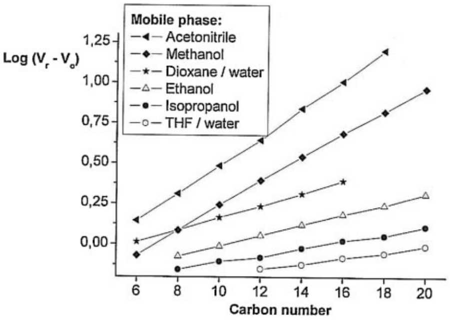

***Figure 1.***
Dependence of retention of n-alkanes on the carbon number in various mobile phases.[16] $V_r$ – retention volume; $V_o$ – void volume (volume of liquid in the column).

A persuasive example of the separation power of HPLC is shown in Figure 2. Isomers of nonane have been separated by adsorption mechanism. The retention of isomers is seen to depend on the number of methyl groups and as well as their position within the chains. The result in Figure 2 implies that branched polyolefins should be less adsorptive than linear chains under these conditions. The same trend has been found by Möckel et al.[31].

The so called critical conditions (Liquid chromatography under critical conditions - LCCC) for a polymer correspond to the condition where one specific type of polymer chains is eluted at the constant elution volume independent of the molar mass. At first sight, it seems that this effect can not be useful for polymer separation. However, many authors have demonstrated the opposite.[38–40] Under the critical conditions of one type of polymer, polymers of other types will elute at different elution volumes. This enables separation of polymers which differs one from another only slightly in their chemical composition (for example, in the type of end groups, in the number of polar substituents) or in their structure (tacticity, cyclic versus linear and similar).

A number of new and impressive applications of LCCC has been elaborated in the past years[39–45] and they have popularized the LCCC concept in the polymer community. The first LCCC systems for separation of ethylene-styrene and ethylene-methyl methacrylate copolymers at temperature as high as 140 °C have been just recently published.[46,47]

The result in Figure 3 illustrates that Freeman and Killion[28] have been working near to critical conditions (LCCC) for n-alkanes, although at that time the concept of LCCC was unknown. The column used by Freeman and Killion[28], a copolymer of 80% isodecylmethacrylate and 20% divinylbenzene has never been commercially available.

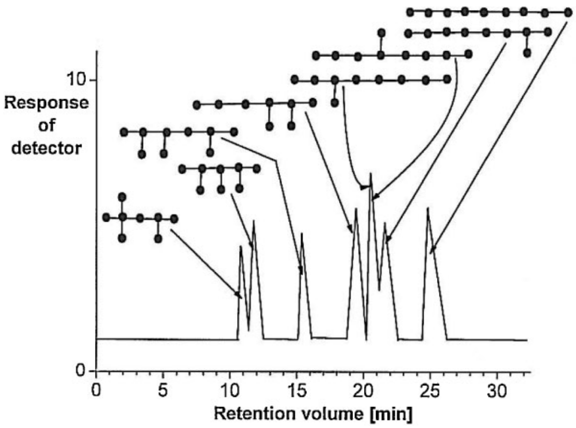

***Figure 2.***
Chromatogram illustrating the separation of branched alkanes. Data reproduced from ref. [33]

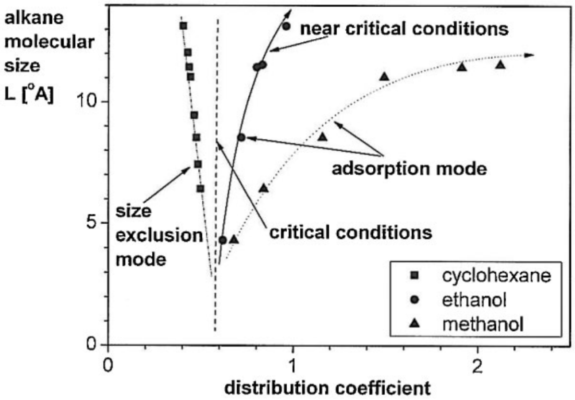

*Figure 3.*
Dependence of the retention on the molecular size of alkanes.[28]

N-alkanes were eluted at constant elution volumes, which is typical for LCCC, in a system described by Wada.[35] Although more than 150 LCCC systems are described in literature[48], a LCCC system for polyolefins is not yet known. This is a challenge for the future, because LCCC could have the potential to separate polyolefins according to their tacticity, chemical composition or topology.

## From HPLC of Alkanes to HPLC of Polyolefins

### Potential Mobile Phases for Liquid Chromatography of Polyolefins

In majority of cases the dissolution of polyolefins requires temperatures of 130–160 °C, thus solvents with higher boiling points are needed for dissolution at atmospheric pressure. Data about the solubility of polyethylene (PE), polypropylene (PP) and other polyolefins are rarely available. A quick way to gain a preliminary information about the thermodynamic quality of a solvent may be obtained by cloud point measurements.[49] As it is illustrated in Figure 4 depending on the solvent used, the cloud point temperatures for linear PE vary in a broad range. Solvents with high cloud point temperature often require prolonged time for the dissolution. We have tested the majority of these solvents as mobile phases and the results are summarised in the following paragraphs.

### Adsorption of Polyolefins on Zeolites

Inspired by the retention of alkanes on zeolites[26], we have found that even PE and PP are strongly retained (adsorbed) on some zeolites, such as SM300, CBV-780, CP814.[50–52] As a consequence, linear PE may be selectively removed from blends with PP in decalin-SM300, while isotactic PP may be removed from blends of PE and PP using the zeolite CBV-780, all at a temperature of 140 °C.[53] In this case PE or PP with very low molar masses as well as with very high molar masses are strongly adsorbed in the zeolites from specific liquids. The dimensions of PE in linear conformation commensurate with the dimensions of pores in zeolites. Accordingly, if the pores of the zeolite are blocked by the adsorbed polymer chains, molecules of solvent can not penetrate and displace the adsorbed macromolecules, i.e., the adsorbed chains of PE and PP can not be desorbed at all. This limits the use of a zeolite column packing, because if all adsorption sites are blocked by the adsorbed macromolecules, the column packing can not adsorb more substance[53,54] and a new zeolite column packing is needed.

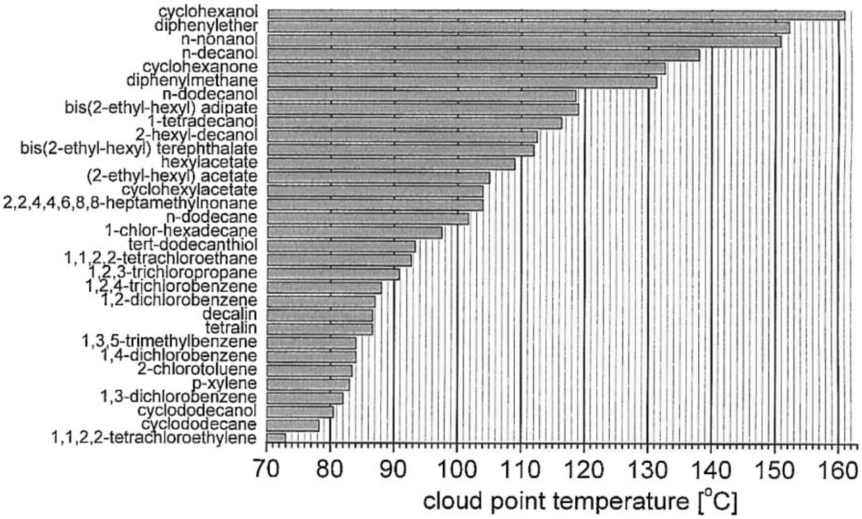

***Figure 4.***

Cloud point temperatures of linear polyethylene with the weight average molar mass 260 000 g/mol (number average molar mass 89 600 g/mol) in various liquids. Data partially published previously.[49]

## Adsorption from Chlorinated Solvents

Following the adsorption of alkanes from perfluorosolvents (Table 2), the retention of PP and PE dissolved in 1,1,2,2-tetrachloroethane and 1,2,3-trichloropropane were measured.[55] PE and PP are retained at a temperature of 135 °C, however, they were partially chlorinated. Moreover, these solvents lead to corrosion in the HPLC instrument, which is not desirable in practice.

## Precipitation liquid chromatography of polyolefins

As illustrated in the previous paragraphs, alkanes have been separated using mobile phases with solvent/nonsolvent pairs, such as methanol/water, acetonitrile/water, etc. These mixed liquids do not dissolve polyolefins and some of them do not dissolve alkanes. In such cases, the alkanes have been injected in a pure solvent. Such conditions lead to precipitation mechanism of separation. Various solvent/nonsolvents have been applied for preparative fractionation (Holtrup fractionation) of polyolefins.[56] Lehtinen and Paukerri[57] have found that ethylene glycol monobutyl ether (EGMBE) dissolves PP, but not PE. It was shown that isotactic PP is separated from linear PE on silica gel modified with chemically bonded oligodimethylsiloxane if EGMBE is used as the mobile phase.[58] The polymers have been injected in TCB, i.e. under so called limiting conditions.[59] The fraction of PE with higher molar masses has been, however, strongly retained in the column and PE was recovered only partially. With a modified system that uses the gradient EGMBE-TCB as the mobile phase and 1-decanol as the sample solvent, a HPLC system has been found, which separated PE from PP more efficiently[60,61] than the previous system. PP, which is soluble in EGMBE has been eluted isocratically, while PE have been precipitated in the silica gel column and eluted finally in a linear gradient of EGMBE/TCB. In addition to blends of PE and PP, ethylene-propylene copolymers have been separated in this way according to their chemical composition for the first time.[61]

## Reversible Adsorption Liquid Chromatography of PE and PP

The retention of n-alkanes was most often found, when an alcohol has been used as the mobile phase. Results by Möckel et al.[31] indicate that n-alkanes are more strongly retained on a carbon column than on silica gel C18, when methanol was used as the eluent. The dissolution of PE and PP require an alcohol with a high boiling point. The screening of the solubility of PE by the described procedure[49] revealed that n-decanol could be a suitable alcohol. Several standards of linear PE, atactic, isotactic and syndiotactic PP have been dissolved in n-decanol and injected into a carbon-based column. The results are shown in Figure 5. Only peak corresponding to i-PP appeared in the chromatogram. The other components have been fully retained (adsorbed) in the column. After gradient elution with TCB, three additional peaks eluted (Figure 5). We summarise that the mentioned sorbent-solvent pair enables to separate linear PE from PP, as well as separation of PP according to its tacticity. A detailed description of these measurements will be published separately.[63]

Current standard separation of the mentioned polyolefins include TREF, CRYSTAF or Holtrup fractionation. These methods require larger amounts of solvents and time, in comparison with a HPLC method. The described HPLC system enables a faster and more selective separation. It could be used for high-throughput analysis and characterization of polyolefins in research and development laboratories.

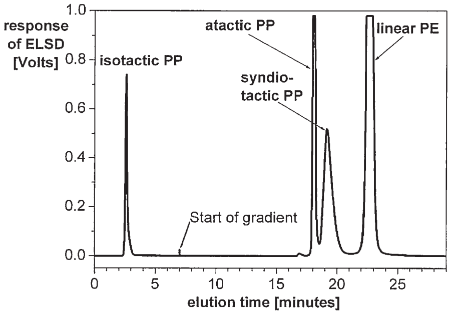

*Figure 5.*
Chromatogram obtained after the isocratic and gradient elution. Mobile phase and sample solvent: n-decanol. Gradient: From 100% n-decanol to 100% 1,2,4-trichlorobenzene in 10 minutes. Temperature: 160 °C. Flow velocity: 0.5 ml/min. ELSD – evaporative light scattering detector. Peaks in the chromatogram correspond to isotactic polypropylene (weight average molar mass 200 000 g/mol), atactic polypropylene (315 000 g/mol), syndiotactic polypropylene (196 000 g/mol) and 5 samples of linear polyethylene (14 000 - 260 000 g/mol).

## Conclusion

Molecules of alkanes of $C_{6-40}$ are very small in comparison with PE macromolecules. Similarly like behaviour of children and adults are interrelated, the elution behaviour of alkanes and PE chains is interconnected. Knowledge of the elution behaviour of alkanes at room temperature is helpful, as it was shown here, for the identification of suitable solvent-sorbent pairs for the separation of polyolefins at high temperature. Although the differences in the chemical composition or structure of polyolefins are often very small, further sensitive HPLC separation systems may be certainly discovered. If the development of interactive liquid chromatography will be adequately sponsored, then in no more than 10 years from now, it might be a standard method for separation of polyolefins according to their chemical composition, tacticity and branching, just like the high temperature SEC is the first choice, when the values of the molar mass are requested.

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