

Adsorption of polyethylene standards from decalin on liquid chromatography column packings

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Abstract

Linear polyethylene and isotactic polypropylene standards were injected into columns which contained MFI (SH-300 and silicalite) or faujasite (CBV-780) type zeolites. 1,2,4-Trichlorobenzene, cyclohexanone, 2-ethyl-hexanol, decalin and tetralin were used as mobile phases at 140 °C. It was found that polyethylene is fully retained on zeolite SH-300 when decalin is used as a mobile phase. Moreover, polyethylene is partially retained on zeolite SH-300 from tetralin and from 1,2,4-trichlorobenzene, on silicalite from decalin and in a very small extent on zeolite CBV-780 from decalin. Using all other solvents, polyethylene and polypropylene were not retained in any of the columns tested. This is the first experimental observation of polyethylene adsorption from a solvent on a chromatographic stationary phase.

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1. Introduction

Approximately 52 million tons of polyethylene (PE) were produced world-wide in 2000 [1]. PE copolymers also form a significant proportion of the world-wide production, and polypropylene (PP) is used as the major comonomer. Due to their significant commercial importance, polyethylene materials are intensively studied. Generally, PE and PE copolymers have a semicrystalline structure. As a result, they are soluble only in certain solvents and only at elevated temperatures (as high as 140–160 °C). PE materials represent mixtures of non-

polar macromolecular chains with different molar masses. PE containing copolymers can vary not only in molecular architecture but also in chemical composition.

Several methods are established for the analytical characterization of such polymers [2]. Molar mass distribution of PE materials is routinely determined by high temperature size exclusion chromatography (HT-SEC). 1,2,4-Trichlorobenzene is commonly used as the mobile phase and polystyrene–divinylbenzene gels as the column packing, both at a temperature of 135–145 °C [3]. Branch type distribution in polyolefins is characterized by temperature rising elution fractionation (TREF) and crystallization fractionation (CRYSTAF) [4]. For characterization of the branching distributions in PE as a function of molar mass, HT-SEC coupled to a molar-

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mass-sensitive detector is used. This set-up enables the evaluation of long chain branching (see, e.g. [5]) as a function of molar mass, while HT-SEC coupled to infrared spectroscopy or NMR is applied for evaluation of short chain branching [6]. Fractional precipitation is used for preparative fractionation of these materials [7].

Commercially important synthetic polymers, such as polystyrene or polymethylmethacrylate, may be analyzed by size exclusion chromatography (SEC), or by adsorption liquid chromatography [8–10]. For polyethylene, however, only the SEC mode is available. No sorbent–solvent system is presently known, which enables adsorption of polyethylene chains. An adsorption system would be attractive and useful, especially for the chromatographic characterization of PE and PP in polymer blends and for HPLC separation of PE copolymers according to their chemical composition. SEC can not distinguish between chemically different polymer chains. On the other hand, adsorption phenomena depend very sensitively on the chemical composition of a solute.

Polyethylene is a mixture of alkanes of high molar masses. Alkanes up to C_5 – C_9 are retained on silica gel C_{18} column packings from polar solvents, such as methanol–water [11]. A pronounced retention of alkanes was observed when a silicalite was used as the column packing and methanol as the mobile phase [12]. Polyethylene is not soluble in such polar liquids. Denayer et al. [12] have found that alkanes up to C_{16} were retained in columns packed with different types of zeolites. Zeolites are crystalline materials built up of SiO_4 and AlO_4 tetrahedra, joint together in regular arrangements to form an open structure with pores of molecular dimensions [13]. With zeolite ZSM-5, C_7 – C_{16} alkanes were retained when *n*-hexane or *n*-octane was used as the mobile phase at room temperature. The retention of alkanes significantly increased with their molar masses. An increased retention of some branched alkanes on the ZSM-5 was also found [12]. These findings indicate that a retention of PE or PP is possible, when a specific mobile phase, which is compatible with PE or PP, can be selected.

In this paper, the retention behavior of polyethylene and polypropylene on ZSM-5 and faujasite type zeolites is qualitatively described.

2. Experimental part

2.1. Solvents

1,2,4-Trichlorobenzene, decalin, tetralin, 2-ethyl-1-hexanol, cyclohexanone, all of synthesis quality (Merck, Darmstadt, Germany) were used in this study.

2.2. Polymers

Linear PE standards were purchased from Polymer Standards Service, Mainz, Germany. Their peak molar masses were 1.08; 2.03; 22; 66; 145 $kg\ mol^{-1}$, polydispersities were in the range 1.11–1.72. Isotactic PP samples of 32.6 $kg\ mol^{-1}$ and PP 57 $kg\ mol^{-1}$ (polydispersity 2.6 and 2.1, respectively) were prepared in the Department of Chemistry, University of Stellenbosch, South Africa [14]. Linear PE and isotactic PP with weight average molar mass of 500 and 200 $kg\ mol^{-1}$, respectively, were obtained from PSD Polymers, Linz, Austria, the polydispersity was around 3.

PE and PP standards were dissolved at 160 °C (1.5 h, with occasional agitation) in the corresponding mobile phase. When using 2-ethyl-1-hexanol PE was injected in cyclohexanone due to the limited solubility of PE in 2-ethyl-1-hexanol. An antioxidant was not added to the sample solution because the antioxidant (Irganox 1010) was detected as a significant peak on the chromatogram. It was assumed that extent of polymer degradation through the measurement is small and may be neglected. The mobile phase was filtered three times (filters are parts of HPLC assembly used), in the eluent container, before the pump and the column.

2.3. Column packings

HPLC columns were prepared by manual packing of zeolite crystals into stainless steel columns with an internal diameter of 4.6 mm. Two columns were packed with MFI type zeolites. The pore system of MFI contains linear channels with a free pore diameter of $5.6 \times 5.3\ \text{Å}$, intersecting with sinusoidal channels, having a free diameter of $5.5 \times 5.1\ \text{Å}$. The first 150 mm column contained silicalite (Alsi-Penta

Zeolithe GmbH, Schwandorf, Germany), with a Si–Al ratio of 400. This material has a particle size larger than 10 μm . The second column, with a length 150 mm, contained zeolite SH-300 (Alsi-Penta product), a ZSM-5 material with a Si–Al ratio of 150. SH-300 has an average particle size of about 10 μm . A column with a length of 50 mm was filled with an Ultra Stable Y zeolite, USY CBV-780 (Zeolyst Int., Valley Forge, PA, USA), with a Si–Al ratio of 40. This zeolite contains free cavities with a diameter of 12 Å. These cavities are connected through windows with a size of 7.3 Å. This zeolite also contains larger mesopores, with a size between 40 and 400 Å [15]. Most of the mesopores are present as cavities rather than cylindrical pores connecting the external surface with the interior of the crystallite [15]. The CBV-780 crystals have an irregular spherical morphology, with an average particle size of 0.5 μm .

The sorption properties of the used column packing materials were described by Denayer et al. [12]. Generally, the higher the Si–Al ratio of a zeolite is, the more hydrophobic it behaves.

2.4. HPLC Assembly

A high temperature liquid chromatograph Waters 150C (Waters, Milford, USA) was connected with an

evaporative light scattering detector (ELSD), model PL-ELS 1000 (Polymer Laboratories, Shropshire, UK). The nebulizer temperature was set to 200 °C, the evaporator temperature was 270 °C, and the gas flow-rate 0.5 standard l min^{-1} . The temperature of the autosampler and the column oven was maintained at 140 °C. Fifty μl of the polymer solutions were injected. The polymer concentration was around 0.5 mg ml^{-1} . The flow-rate of the mobile phase was 0.4 ml min^{-1} (column length 50 mm) or 1.0 ml min^{-1} (column length 150 mm).

3. Results and discussion

Table 1 summarizes the elution behavior of PE and PP standards in the tested column packing–mobile phase systems. PE standards were eluted from all columns when the mobile phase consisted of cyclohexanone or 2-ethyl-1-hexanol. PP eluted from all columns and all eluents. In these cases, PE and PP were eluted at constant elution volumes (SH-300 and silicalite column) or the elution volumes decreased gradually with increase of the average molar masses (CBV-780 column).

When, however, the column packed with zeolite SH-300 was used, PE standards were fully retained

Table 1
Survey of elution behavior of polyethylene and polypropylene standards

Column packing	Mobile phase	Polyethylene	Polypropylene
Silicalite Si–Al=400 Pores 5–6 Å	1,2,4-trichlorobenzene	Eluted	Eluted
	Cyclohexanone	Eluted	Eluted
	2-ethyl-1-hexanol	Eluted*	Eluted
	Decalin	Partially retained	Eluted
SH-300 Si–Al=150 Pores 5–6 Å	Tetralin	Eluted	Eluted
	1,2,4-trichlorobenzene	Partially retained	Eluted
	Cyclohexanone	Eluted	Not measured
	2-ethyl-1-hexanol	Eluted*	Eluted
CBV-780 Si–Al=40 Pores 7–12 Å Mesopores 40–400 Å	Decalin	Fully retained	Eluted
	Tetralin	Partially retained	Eluted
	1,2,4-trichloro-benzene	Eluted	Eluted
	Cyclohexanone	Eluted	Eluted
Mesopores 40–400 Å	2-ethyl-1-hexanol	Eluted*	Eluted
	Decalin	Partially retained	Eluted
	Tetralin	Eluted	Eluted

*PE injected after dissolution in cyclohexanone.

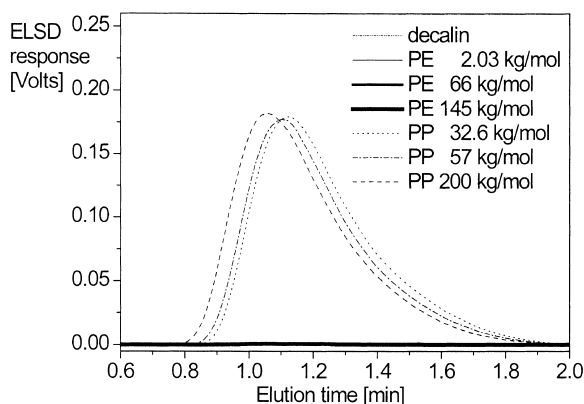


Fig. 1. Chromatograms of polyethylene and polypropylene samples injected in decalin. Mobile phase: Decalin. Column packing: Zeolite SH-300. Temperature: 140 °C.

from decalin. Fig. 1 shows chromatograms of the PE and PP samples. The peaks shown correspond to PP, while there are no PE peaks due to full adsorption of polyethylene to the zeolite.

When the silicalite column was used with decalin as the mobile phase, the height of the PE elution peaks increased with increasing molar mass (see Fig. 2). For proving the adsorption of PE, the same solutions were injected into the system without the column. In this case, all elution peaks had almost the same peak height. Accordingly, the decrease in the elution peak heights when the column is used, can only be attributed to adsorption of PE on the

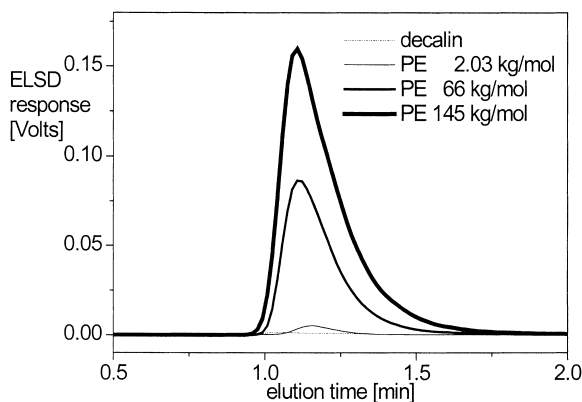


Fig. 2. Chromatograms of polyethylene samples injected in decalin. Mobile phase: Decalin. Column packing: Silicalite. Temperature: 140 °C.

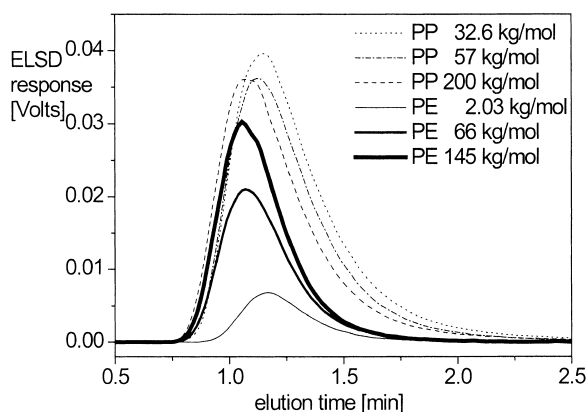


Fig. 3. Chromatograms of polyethylene and polypropylene samples injected in tetralin. Mobile phase: Tetralin. Column packing: Zeolite SH-300. Temperature: 140 °C.

stationary phase. Adsorption of PE on silicalite from decalin as the mobile phase is less pronounced as compared to SH-300.

Partial adsorption of polyethylene was also observed on zeolite SH-300 from tetralin (Fig. 3) and from 1,2,4-trichlorobenzene (Table 1). Differently from zeolite SH-300 and silicalite, zeolite CBV-780 contains mesopores 40–400 Å. PE and PP are eluted from the CBV-780 column as it is usual in size exclusion mode (Fig. 4). The height of PE peaks should be similar, however, their heights increase with molar masses of PE samples (Fig. 4), similarly as it is the case in Figs. 2 and 3. It indicates that PE

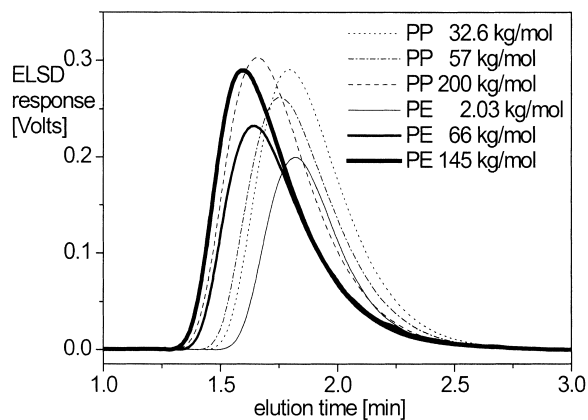


Fig. 4. Chromatograms of polyethylene and polypropylene samples injected in decalin. Mobile phase: Decalin. Column packing: Zeolite CBV-780. Temperature: 140 °C.

is in a small extent retained in the zeolite CBV-780 when decalin is used as the mobile phase.

Decalin is thermodynamically a very good solvent for PE. Precipitation of PE on the sorbent particles should thus not occur. Therefore, we suspect that attractive (adsorptive) interactions between the zeolite surface and the PE chains in decalin are responsible for the retention. Zeolite SH-300 has almost identical properties as the ZSM-5 sorbent used in Ref. [12]. The retention of C_7 – C_{16} n -alkanes increased with their molar mass with this type of zeolite when n -octane was used as the mobile phase [12]. The n -alkanes with much higher molar masses (PE) are fully adsorbed from decalin, as it is illustrated in Fig. 1. PE with a weight average molar mass as high as 500 kg mol^{-1} was also fully retained from decalin in the SH-300 column packing.

Taking into account that the internal pores of the zeolite SH-300 are only 5–6 Å wide, the question arises whether the PE chains are adsorbed inside these pores or on the external surface of the zeolite. Assuming that a solvated macromolecule has a hypothetical spherical shape, it is possible to calculate the corresponding radius of this sphere, denoted as radius of gyration R_g according to Eq. (1) [16]:

$$R_g = \sqrt[3]{\frac{[\eta] \cdot M}{\Phi'}} \quad (1)$$

where $[\eta]$ is the intrinsic viscosity of the polymer in a certain solvent and at a certain temperature and M is the polymer molecular mass. Flory's universal

constant Φ' is taken to be 3.1×10^{24} (with $[\eta]$ in ml g^{-1}). Eq. (1) was derived for linear polymers in a theta solvent [16]. The intrinsic viscosity $[\eta]$ was calculated from the Mark–Houwink–Sakurada equation:

$$[\eta] = K \cdot M^a \quad (2)$$

The corresponding constants a , K and the calculated radius of gyration are summarized in Table 2.

The tabulated Mark–Houwink–Sakurada constants a , K for PE from literature are often significantly different [20], although they correspond to the same solvent. Thus, the calculated radius may also vary according to the constants used. But in any case the radii of gyration of the spherical coils (Table 2) are much larger than the pore diameters of the zeolites. Adsorption inside the pores requires a substantial change in the conformation of the PE chains (from random coils to approximately linear conformations) and their penetration into these pores. PE chains with smaller molar masses may change their chain conformations easier, moreover, they diffuse faster and thus penetrate easier into the pores. As a result, smaller chains may be adsorbed to a more significant extent than larger chains. This seems to be in agreement with Fig. 2, i.e., where the polyethylene samples with smaller molar masses have smaller recovery.

Thermodynamic quality of a solvent can be estimated also from the Mark–Houwink–Sakurada equation (Eq. (2)), where K and a are constants for given polymer–solvent system. In a good solvent

Table 2
The calculated radius of gyration of polyethylene

Mobile phase	Polyethylene (low pressure)					
	T (°C)	a	K (ml g^{-1})	Ref.	M (kg mol^{-1})	R_g (Å)
1,2,4-trichlorobenzene	135	0.706	0.051	[17]	2	19
					66	140
					145	219
Decalin	135	0.73	0.046	[18]	2	19.7
					66	148
					145	233
Tetralin	130	0.725	0.051	[19]	2	20
					66	150
					145	236

and for flexible polymer coils, the value of unitless constant k' lies in the range of 0.75. The decrease of k' down to 0.5 indicates the shrinkage of polymer coils due to decreased thermodynamic quality of solvent. Adsorption of PE is observed exclusively from thermodynamically very good solvents for PE (see coefficients k' in Table 2). This fact supports proposition that PE chains partially enter the pores of the zeolites. Namely, in such solvents polymer coils expand and prolongation of chains, which is necessary for their diffusion into narrow pores, occurs with higher probability.

Comparing the Si–Al ratios of the tested column packings, zeolite CBV-780 (Si–Al=40) is the less hydrophobic, i.e. exhibits the most polar character. This could be a reason why CBV-780 does not show adsorption of PE and PP in all tested mobile phases (Table 1), except a decreased PE recovery in decalin–SH-300 (Fig. 4).

Silicalite (Si–Al=400) must be more hydrophobic than the zeolite SH-300 (Si–Al=150), although the difference might be small. In agreement with the hydrophobicity, alkanes C_5 – C_{10} were adsorbed to larger extent on silicalite compared to SH-300 [9]. However, the opposite effect is observed for adsorption of PE from decalin, i.e. PE is fully adsorbed on zeolite SH-300 and only partially on silicalite. Therefore, the Si–Al ratio seems not being the key determinant of adsorption. An additional, yet unknown parameter of the used column packings probably plays a role in adsorption of PE.

Partial adsorption of PE is also observed when the column packed with SH-300 is flushed with tetralin (Table 1). A small increase of the polarity of the mobile phase (tetralin–contra decalin) decreases the extent of adsorption of PE in the SH-300 column (the partial adsorption from tetralin contra the full adsorption from decalin). We suspect that using 1,3,5-trichlorobenzene as the mobile phase would lead to full adsorption of PE, because using of 1,2,4-trichlorobenzene causes the partial adsorption of PE (Table 1).

A larger increase of the polarity of the mobile phase leads to full elution of PE. As shown in Table 1, PE is not retained from 2-ethyl-hexanol or cyclohexanone on any column packing. Probably, the thermodynamic quality of these polar solvents (i.e., poor solvents for PE and PP) does not favor change of conformation from random coils to approximately

linear shapes. Change of conformations is, however, important for an effective penetration and adsorption.

According to previous measurements [9], polar molecules like acetone and cyclohexanol are retained on the surface of ZSM-5 from *n*-octane (partition coefficient 2.38 and 1.29). Since there is a very high concentration of cyclohexanone and 2-ethyl-1-hexanol present when they are used as mobile phase, pore blocking by solvents cannot be ruled out completely. This would prevent PE chains entering the pores, explaining the effect of solvent polarity on the retention of the polymers.

The retained PE is not removed from the column packed with SH-300, when it is flushed with cyclohexanone at 140 °C, indicating that adsorption of PE is very strong. This suggests that at least a part of the PE chain is adsorbed in the pores, and not only on the external surface, for which irreversible adsorption is not expected. Possibly, other types of zeolites could enable a reversible adsorption.

Adsorption capacities for *n*-alkanes (C_5 – C_{22}) are between 0.11 and 0.17 ml g⁻¹ (corresponding to 85–144 mg hydrocarbon per 1 g of zeolite). Our preliminary test shows that the adsorption capacity of a 50-mm SH-300 column is about 2 mg of PE 53.1 kg mol⁻¹ in decalin as the mobile phase. This corresponds to a capacity of about 2.5 mg g⁻¹ zeolite (there was 0.8 g of the zeolite in this column). After adsorption of this amount of PE into the adsorbent, PE is not further adsorbed, i.e. PE elutes from the column. The adsorption capacity seems quite low at first sight compared to the adsorption capacity for *n*-alkanes, so we suppose that the PE molecules only adsorb close to the external surface of zeolite SH-300 and do not reach the pores in the center of the crystals.

We have injected only 0.025 mg PE per injection, what means that the small column (50×4.6 mm) may adsorb PE from about 100 injections. The larger column (150×4.6 mm) has a larger adsorption capacity (~300 injections). If necessary, the adsorbed PE may be removed by burning in air at 500–550 °C without destroying the original structure of the zeolite.

PP is not retained in the zeolites with the pore diameters 5–6 Å. Cavalcante and Ruthven [21] have measured intracrystalline diffusivities of several methyl-branched isomers of hexane in silicalite and it was shown that diffusivity substantially decreased

in order: linear > single-branched > double branched. PP chains, which contain many methyl branches, undergo probably a large diffusional barrier compared to linear macromolecules and therefore are not retained in the SH-300 column and in the silicalite column. PP is, however, not retained also in the zeolite with the larger pore diameters, i.e. CBV-780. CBV-780 contains also larger mesopores, with a size between 40 and 400 Å [15]. Such pores are sterically accessible for coils of PP, what manifest itself in elution of PP in size exclusion mode (Fig. 4). The adsorbent CBV-780 is the most polar from the tested zeolites. The polar character of CBV-780 is probably responsible for free elution of PP in all solvents tested.

It is known that *n*-alkanes ([12,22] and references there) penetrate into pores of 5–6 Å. Namely, these pore diameters in zeolites SH-300 and silicalite are comparable with the cross-section of 4.9 Å of a linear alkane molecule [22]. Normal alkanes are retained in zeolites due to dispersion forces where the sorbent–sorbate interactions is proportional to the polarizability of the sorbate [23]. Such an interaction is pronounced for highly polarizable molecules such as large hydrocarbons. Chains confined in narrow pores may have a much larger number of intensive contacts with the pore walls in comparison with chains that are adsorbed only on the surface of zeolite particles. We suppose that if the attractive interactions between pore walls and PE chains are large enough, a partial penetration of PE chains could enable full retention of PE in some zeolites. Theoretical Monte Carlo simulations for macromolecules, which have a radius of gyration larger than the pore diameter, have shown that a polymer chain may be partially adsorbed inside of the pores and partially outside of the pores. The chain part inside the pore stretches out considerably while the remaining part outside the pore is coil-like ('flower-like conformations') [24]. The smallest ratio R_g –pore radius considered in the study by Hermesen et al. [24] was 1.6. Interaction of much larger unipolar macromolecules with zeolites was, according to our knowledge, not yet studied either theoretically or experimentally.

4. Conclusion

A column packing–solvent system was described,

in which polyethylene is fully retained. Adsorption of polymers on a sorbent surface from a solvent is a known phenomenon. The adsorption of polyethylene is according to our knowledge, however, experimentally observed for first time in the present work.

Polyethylene chains represent fully non-polar macromolecules. Decalin is a thermodynamically very good solvent for these molecules, with a non-polar character. Thus, the strong retention of polyethylene chains in a zeolite with pore diameters as small as 5–6 Å, is quite surprising.

In HPLC and SEC of polymers, the pore diameters of the column packings are larger or comparable to the dimensions of the solvated macromolecular coils in solution. With zeolites, where full or partial retention of polyethylene was observed, the pore diameters are comparable to the cross-section of the linear macromolecular chains. Thus, interactions between the pore walls and the polymer chain inside the pores may be more intensive. Moreover, the accessibility of the pores may depend on the structure of the chains (branched contra linear chains, i.e. polypropylene contra polyethylene). A better understanding of the described phenomenon requires a more detailed study.

The presently described sorbent–solvent adsorption system for polyethylene could open access to realization of adsorption chromatography of polyolefines. Further research has to be conducted to identify a combination of a zeolite and a mobile phase, enabling a reversible adsorption of PE.

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