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Influences of surface chemistry on the separation behavior of stationary phases for reversed-phase and ion-exchange chromatography: a comparison of coated and grafted supports prepared by ring-opening metathesis polymerization

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Abstract

A series of poly(norborn-2-ene) (poly-NBE), poly(7-oxanorborne-2-ene-5,6-dicarboxylic acid) (poly-ONDCA), as well as poly(norborn-2-ene-co-7-oxanorborne-2-ene-5,6-dicarboxylic acid) (poly-NBE-co-ONDCA) based silica supports were prepared via ring-opening metathesis polymerization (ROMP) using both coating and grafting techniques. Poly-NBE-grafted and poly-NBE-coated supports were used for the reversed-phase separation of phenols; poly-NBE, poly-ONDCA as well as poly-NBE-co-ONDCA-grafted supports were used for comparative studies on the separation of a series of anilines and lutidines. As expected, grafted supports possess superior separation capabilities compared to their coated analogues. Compared to pure poly-NBE- and poly-ONDCA-grafted stationary phases, supports consisting of poly-NBE-co-ONDCA block-copolymers possess both hydrophobic and ion-exchange sites and represent optimum stationary phases for the separation of isomeric basic analytes. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polymer grafting represents a well-established and useful procedure for the preparation of certain polymer architectures [1–3]. It may be accomplished by many polymerization techniques, e.g., metathesis polymerization [4], atom-transfer radical polymerization [5], Ziegler–Natta [6] or cationic ring-opening polymerization [7] and carried out either homoge-

neously, heterogeneously or from the gas phase [8]. In terms of surface grafting, mainly styrene- and acrylate-based resins have been used so far [1,9]. Despite all progress and advantages, grafted supports often suffer from insufficient pH stability. One approach that circumvents these problems is the use of soluble prepolymers for coating. This technique has been reported as early as in 1987 by Kolla et al. who prepared poly(butadiene-*block*-maleic acid)-coated silica columns for ion chromatography [10]. Later, Läubli and Kampus reported on poly-maleic acid-based columns with improved durability [11,12]. Optimum deposition conditions [13] have also been developed for pure hydrophobic coatings

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of silica [14–18]. Unfortunately, this technique often results in a significant loss of surface area (σ) due to pore clogging [19]. In this context, Kurganov et al. [20] demonstrated that especially micro- and mesoporous materials show a significant loss in pore volume and specific surface, e.g., after coating with a polystyrene–diethoxysilane copolymer which was attributed to pore narrowing owing to the polymer immobilization. Ring-opening metathesis polymerization (ROMP) has been successfully introduced by our group for the synthesis of a large variety of tailor-made supports suitable for solid-phase extraction (SPE) [21–27], capillary electrophoresis (CE) [28], high-performance liquid chromatography (HPLC) [19,29] as well as hyphenated techniques [30,31]. Various approaches such as precipitation polymerization [32], coating [19] or grafting techniques [4] have been applied for these purposes. Recently, even functionalized monolithic separation media have become accessible by this approach [33,34]. The general opportunity to synthesize supports that consist of block-copolymers at the surface and the possibility to design such block-copolymers in terms of block-size allow more detailed mechanistic studies on certain separations on both coated and grafted carriers. In this contribution we report on the differences between coated and grafted silica-based supports in the reversed-phase (RP) separation of phenols as well as on the influence of the backbone polarity and pH on the separation of isomeric anilines and lutidines.

2. Experimental

General experimental details and instrumentation [including Brunauer–Emmett–Teller (BET) measurements] are described elsewhere [4]. Stainless steel HPLC columns (150×2 mm) were purchased from GROM Analytik+HPLC (Herrenburg, Germany). Silica materials (Purospher STAR, 5 μm , 120 \AA) were purchased from Merck (Darmstadt, Germany), norborn-2-ene-5-yltrichlorosilane was purchased from ABCR (Karlsruhe, Germany). Azobis-*i*-butyronitrile (AIBN) was purchased from Aldrich (Vienna, Austria). 7-Oxanorborn-2-ene-5,6-dicarboxylic anhydride [35,36] was prepared accord-

ing to literature procedures and checked for purity by means of nuclear magnetic resonance (NMR) spectroscopy. The initiator $\text{Cl}_2\text{Ru}(\text{PCy}_3)_2(\text{CHC}_6\text{H}_5)$ (Cy=cyclohexyl) was purchased from Fluka. All purchased starting materials, HPLC solvents as well as the investigated compounds were used without any further purification. The synthesis of norborn-2-ene derivatized silica is described elsewhere [4]. The average number of norborn-2-ene units attached to the surface of Purospher STAR was 0.74 mmol/g. The synthesis of poly(norborn-2-ene) (poly-NBE) for coating purposes is described elsewhere [19].

2.1. Silanization of silica with norborn-2-ene-5-yl-methylchlorosilane (preparation of NOR-silica)

The corresponding silica was refluxed for 7 h in toluene using a Dean–Stark apparatus in order to remove all water. Toluene was removed, and silanization (6 g silica) was carried out under reflux in methylene chloride (150 ml) using norborn-2-ene-5-yltrichlorosilane (1.25 g, 5.48 mmol) and triethylamine (TEA) (2.98 g, 29.4 mmol). A reaction time of 6 h was found suitable. Elemental (carbon) analysis of an aliquot gave an average norborn-2-ene content of 0.74 mmol/g. Finally, a mixture of dichlorodimethylsilane (0.44 g, 3.4 mmol) and chlorotrimethylsilane (0.71 g, 6.57 mmol) was added, and stirring was continued overnight. After addition of 15 ml methanol stirring was continued for 15 min. The silylated silica was filtrated, washed with methylene chloride, and dried in vacuo.

2.2. Grafting of silica with norborn-2-ene

NOR-Si-silica (2.985 g) was suspended in 10 ml of dimethylformamide (DMF) and $\text{Cl}_2(\text{PCy}_3)_2\text{-Ru}(\text{CHPh})$ (30 mg, 0.036 mmol) was added. After stirring the mixture for 10 min at 65°C, norborn-2-ene (0.449 g, 4.77 mmol) was added and stirring was continued at 65°C overnight. Polymerization was terminated by addition of 1-hexene. Finally, the product was washed with DMF, methylene chloride, methanol and diethyl ether and dried in vacuo. The amount of norborn-2-ene was determined by elemental (carbon) analysis (1.23 mmol/g).

2.3. Grafting of silica with 7-oxanorborn-2-ene-5,6-dicarboxylic anhydride

NOR-Si-silica (3.076 g) was suspended in 10 ml of DMF and $\text{Cl}_2(\text{PCy}_3)_2\text{Ru}(\text{CHPh})$ (30 mg, 0.036 mmol) was added. After stirring the mixture for 10 min at 65°C, 7-oxanorborn-2-ene-5,6-dicarboxylic anhydride (0.453 g, 2.73 mmol) was added and stirring was continued at 65°C overnight. Polymerization was terminated by addition of 1-hexene. Finally, the product was washed with DMF, methylene chloride and diethyl ether and dried in vacuo. The amount of 7-oxanorborn-2-ene-5,6-dicarboxylic anhydride was determined by elemental analysis (0.25 mmol/g).

2.4. Grafting of silica with norbornene and 7-oxanorborn-2-ene-5,6-dicarboxylic anhydride

NOR-Si-silica (0.697 g) was suspended in 10 ml of DMF and $\text{Cl}_2(\text{PCy}_3)_2\text{Ru}(\text{CHPh})$ (30 mg, 0.036 mmol) was added. After stirring the mixture for 10 min at 65°C, NBE (24.4 mg, 0.26 mmol) and 7-oxanorborn-2-ene-5,6-dicarboxylic anhydride (42.8 mg, 0.26 mmol) were added and stirring was continued at 65°C overnight. Polymerization was terminated by addition of 1-hexene. Finally, the silica was washed with DMF, methylene chloride and diethyl ether and dried in vacuo. The total amount of block copolymer grafted onto the surface as determined by elemental analysis and titration (see below) consisted of ONDCA (0.11 mmol/g) and NBE (0.30 mmol/g).

2.5. Preparation of polymer solutions

Distilled tetrahydrofuran (THF) was used throughout. After work-up, polymers were stirred in THF for 2–3 days in order to be dissolved completely. In case of ONDCA-based polymers, any hydrolysis of the anhydride during work-up had to be prevented, since this significantly aggravates or even impedes subsequent dissolution in THF.

2.6. Coating procedure

Poly-NBE (300 mg, $M_r=110\,000$, $M_n=34\,100$, polydispersity (M_w/M_n) (PDI)=3.22) was dissolved in 150 ml CH_2Cl_2 , AIBN (30 mg, 0.183 mmol) and

1.92 g NOR-Si-silica were added and stirred for 1 h. The solvent was evaporated slowly (approximately 50 ml/h). Finally, cross-linking was carried out at $T=120^\circ\text{C}$ over 15 h.

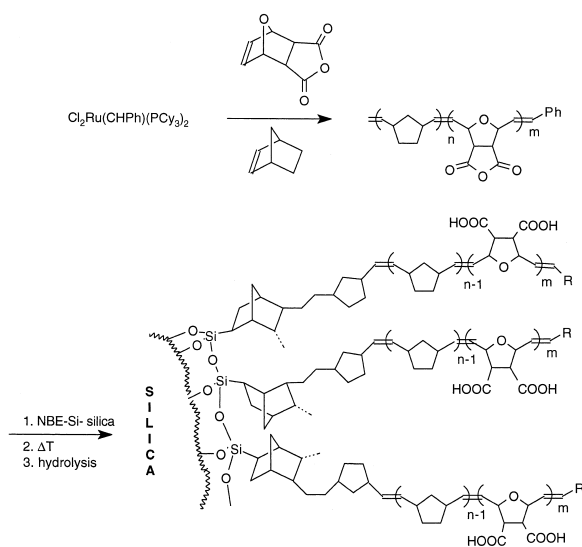
2.7. Determination of capacity

A 200-mg amount of the corresponding coated material (diacid form) was stirred in 10 ml of a 0.05 M aqueous solution of pyridine for 3 h. The resin was filtered off, washed with deionized water and the combined washings were titrated with 0.05 M hydrochloric acid using potentiometric end point indication.

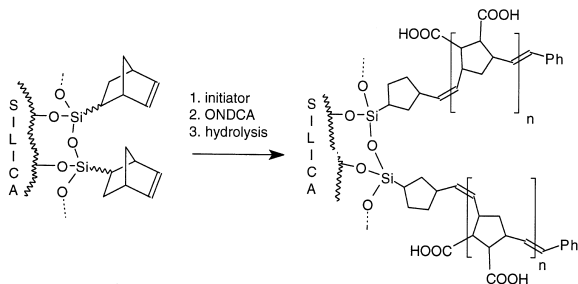
3. Results and discussion

3.1. Synthesis of supports

A detailed description of the grafting [4] and coating [19] procedures of silica using ROMP is given elsewhere. For coating purposes, linear homo- and block copolymers were prepared as described earlier. Silica was dried and reacted with norborn-2-ene-5-yltrichlorosilane in order to obtain polymerizable groups at the surface and to convert as many surface silanol groups as possible to silyl ethers. Different amounts of prepolymer were deposited at the surface and finally cross-linked using thermally initiated radical polymerization (Scheme 1). The general quality of the coating method has already been checked earlier [19] using a standard Engelhardt test [37], which is based on the retention characteristics of a defined mixture of compounds and allows the detection of unwanted silanol–analyte interactions. For that purpose, a simple poly-NBE-coated material was prepared and checked for its retention behavior for various basic and polar analytes. Briefly, a mixture of thiourea, phenol, toluene, ethylbenzene, ethyl benzoate, *N,N*-dimethylaniline, aniline and *m*-toluidine was injected onto the poly-NBE-coated column. Methanol–water (55:45, v/v) was used as a mobile phase. Symmetrical peaks were obtained for all analytes. Additionally, no change in retention time was observed for the basic analytes changing from an unbuffered to a pH 7-buffered mobile phase (1 mM phosphate). Consequently, the



Scheme 1. Synthesis of poly-NBE-co-ONDCA for coating of NOR-Si-silica.



Scheme 2. Synthesis and structure of poly-ONDCA-grafted silica.

poly-NBE-coated material meet the requirements of a “good” column as proposed by Engelhardt et al. [37].

For grafting purposes, dry silica was surface-derivatized with NBE groups. This is easily achieved by reaction of silica with norborn-2-en-5-yltrichlorosilane. The second step consists of the reaction of the initiator ($\text{Cl}_2\text{Ru}(\text{PCy}_3)_2(\text{CHPh})$ ($\text{Cy} = \text{cyclohexyl}$) with the norborn-2-ene-derivatized silica. Finally, the functional monomer is added. The resulting graft-polymer is multiply attached to the support via the norborn-2-ene groups (Scheme 2). Measurements of the specific surface areas (σ) via BET experiments (N_2 adsorption) prior and after grafting revealed that changes in σ were less than 10% in the course of the grafting procedure using micro- and mesoporous silica-based materials, indicating that the pores are not filled with or closed by the corresponding graft-polymer.

3.2. Coated vs. grafted poly-NBE-based supports

Table 1 summarizes the data obtained from the RP separation of six phenols on a poly-NBE-coated (column **I**) and poly-NBE-grafted (column **II**) silica support, respectively. These six phenols were separated on both columns under identical conditions. Column **II** (grafted column) shows higher retention and the reduced plate heights are 3–8-times smaller as on column **I** (coated column). This result can be explained by the loss of specific surface area (σ) during any coating process [19]. This loss has already been described by many authors, e.g., by

Table 1

Results for RP separation of phenols **1–6** on poly-NBE-grafted (column **II**) and poly-NBE-coated (column **I**) silica

No.	Compound	$\text{p}K_a$	Column II			Column I		
			k	N (1/m)	h^a	k	N (1/m)	h
1	Phenol	10.1	2.74	6150	33	2.21	800	250
2	4-Nitrophenol	7.16	5.04	8180	24	3.63	2050	98
3	2-Chlorophenol	9.11	6.02	8610	23	4.96	x^b	x
4	2-Nitrophenol	7.21	8.60	10 100	20	4.96	x	x
5	4-Chloro-3-cresol	9.55	15.5	5890	34	8.38	1820	110
6	2-Methyl-4,6-dinitrophenol	4.34	21.6	12 400	16	10.6	1620	123

^a $h = L \cdot (w_{1/2}/t_R)^2 / [5.54 \cdot d_p]$ (d_p = particle diameter, L = length of column; $w_{1/2}$ = peak half width, t_R = retention time).

^b x = No separation. Conditions: mobile phase water; 30% acetonitrile; 0.1% trifluoroacetic acid. Flow: 0.4 ml/min. Injection volume: 5 μl (2 ppm each). UV (280 nm). Temperature: 25°C.

Unger and co-workers [16,20] and has additionally been studied extensively for a variety of poly-NBE- and poly-NBE-*co*-ONDCA-coated supports [19]. For the present coated systems, we observed a loss of specific surface of roughly 25% as determined by BET. For purposes of illustration, an optimized gradient separation of eight phenols within 15 min on column **II** is shown in Fig. 1.

3.3. Comparison of grafted poly-ONDCA, poly-NBE and poly-ONDCA-*co*-NBE based supports

We already reported on the separation of six isomeric anilines and lutidines within 8 min on poly-NBE-*co*-ONDCA-coated silica supports [19]. Based on the results from RP separations of phenols carried out on coated and grafted supports (see above), we assumed that grafted poly-NBE-*co*-ONDCA-based supports should bring better results since grafting avoids the loss in σ that is entailed with coated supports. Consequently, we synthesized three grafted silica supports based on poly-NBE (column **II**), poly-ONDCA (column **III**) and poly-NBE-*co*-

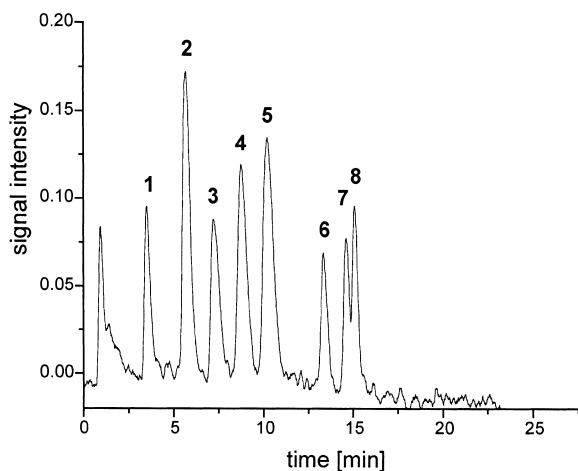


Fig. 1. Gradient separation of phenols **1–8** on column **II**. Conditions: mobile phase: A=water, 30% acetonitrile, 0.1% trifluoroacetic acid; B=acetonitrile, 0.1% trifluoroacetic acid. Gradient: 0% solvent B for 9 min, 0 to 20% solvent B within 5 min, 20 to 25% solvent B within 8 min. Flow: 0.4 ml/min. Injection volume: 5 μ l. UV (280 nm). Temperature: 25°C. 1=Phenol, 2 ppm; 2=4-nitrophenol, 2 ppm; 3=2-chlorophenol, 2 ppm; 4=2-nitrophenol, 1 ppm; 5=2,4-dimethylphenol, 4 ppm; 6=4-chloro-3-cresol, 2 ppm; 7=2,4-dichlorophenol, 2 ppm; 8=2-methyl-4,6-dinitrophenol, 0.4 ppm.

ONDCA (column **IV**). As previously observed for poly-NBE, poly-ONDCA and poly-ONDCA-*co*-NBE coated supports [19], poly-ONDCA-*co*-NBE grafted support (column **IV**) showed the highest number of theoretical plates in the separation of compounds **9–14** compared to the homopolymer-grafted supports poly-NBE silica and poly-ONDCA silica. The same was observed in the separation of the four isomeric hydroxyquinolines **15–18**. Again, optimum separations were achieved on column **IV**. In terms of mechanism (see below), chromatographic sites that are capable of both ion-exchange and RP interactions are believed to play a crucial role in these separations. Fig. 2 shows a representative separation of six isomeric anilines and lutidines within 10 min.

3.4. Separation mechanisms

The results of the separation of the six isomeric anilines and lutidines **9–14** on column **II** are summarized in Tables 2 and 3. The elution order of the amines **9–14** on column **II** is strongly influenced by pH. At pH 9.5 (optimum separation conditions, Table 2), none of the substances is protonated and the elution order (11,13, 10, 9, 14, 12) is a direct result of the different polarities of the analytes. Reduced plate heights (h) of 13–30 are obtained. Since at this

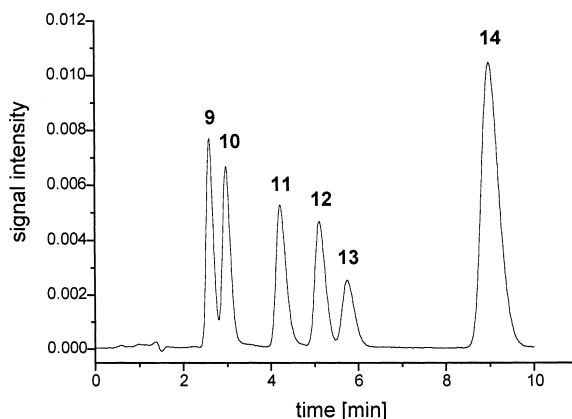


Fig. 2. Separation of isomeric anilines and lutidines **9–14** on column **IV**. Mobile phase: water–acetonitrile–acetic acid– NEt_3 (98:2:0.23:0.60), pH 9.54. Flow: 0.4 ml/min. Injection volume: 5 μ l (5 ppm each). UV (254 nm). Temperature: 25°C. Elution order: 2,6-dimethylaniline (**9**), *N*-methylaniline (**10**), pyridine (**11**), *N,N*-dimethylaniline (**12**), 2,6-lutidine (**13**), 3,4-lutidine (**14**).

Table 2

Comparison of data obtained from the separation of compounds **9–14** on poly-NBE-grafted silica (column **II**) at different pH

No.	Compound	pK_a	Column II ^b			Column II ^a		
			k	N (1/m)	h	k	N (1/m)	h
9	2,6-Dimethylaniline	3.95	5.45	11 600	17	3.92	12 700	16
10	<i>N</i> -Methylaniline	4.82	4.36	10 700	19	3.73	13 100	14
11	Pyridine	5.19	0.98	4110	49	1.42	6850	29
12	<i>N,N</i> -Dimethylaniline	5.15	10.8	17 100	12	6.75	15 700	13
13	2,6-Lutidine	6.99	0.51	3260	61	2.32	8730	23
14	3,4-Lutidine	6.77	1.39	3820	52	3.31	9810	20

^a Conditions: mobile phase: water–acetonitrile–acetic acid– NEt_3 (98:2:0.23:0.60) pH 9.5. Flow: 0.4 ml/min, injection volume: 5 μ l (5 ppm each). UV (254 nm), temperature: 25°C.

^b Conditions: mobile phase: water–acetonitrile–acetic acid– NEt_3 (75:25:0.284:0.48), pH 5.5. Flow: 0.4 ml/min, injection volume: 5 μ l (5 ppm each). UV (254 nm), temperature: 25°C.

pH separation is strictly based on a pure RP mechanism, changes in elution order may serve as a very sensitive tensor for any change in separation mechanism. At pH 5.5, 2,6-lutidine (**13**, $pK_a=6.99$) and 3,4-lutidine (**14**, $pK_a=6.77$) are protonated and are consequently less retained (elution order **13**, **11**, **14**, **10**, **9**, **6**). The situation becomes more complex in the case of poly-ONDCA (column **III**) and poly-NBE-*co*-ONDCA (column **IV**) based supports (Table 3). A comparison of the values for N and h obtained on column **III** under basic and acidic conditions reveals better performance at pH 5.3. The elution order at pH 5.3 (**13**, **11**, **14**, **10**, **9**, **12**) is rather similar to the one found on column **II** at comparable pH. In contrast, a totally reversed order compared to column

II is found at pH 8.4 (**10**, **11**, **9**, **12**, **13**, **14**). This may be expected, since poly-ONDCA-grafted supports are highly hydrophilic and basically do not possess any apolar sites that would be suitable for RP mechanisms. As for poly-ONDCA-grafted columns, poly-NBE-*co*-ONDCA based supports work better under acidic conditions. At a first glance, this may exclusively be attributed to the values of pK_1 (~ 4.1) and pK_2 (~ 5.6) of the ligand. Nevertheless, values for N and h are better by a factor of approximately 2 on column **IV** compared to column **III**. Obviously, the presence of chromatographic sites which are capable of both ion-exchange and RP interactions accounts for the results obtained. In due consequence, such columns shall be suitable for fast

Table 3

Comparison of data obtained from the separation of compounds **9–14** on poly-ONDCA (column **III**) and poly-NBE-*co*-ONDCA (column **IV**) grafted silica at different pH^a

No.	Compound	pK_a	Column III						Column IV					
			pH 8.4			pH 5.3			pH 8.2			pH 5.5		
			k	N (1/m)	h	k	N (1/m)	h	k	N (1/m)	h	k	N (1/m)	h
9	2,6-Dimethylaniline	3.95	1.84	5220	38	3.62	6310	32	2.08	12 700	16	2.69	15 000	13
10	<i>N</i> -Methylaniline	4.82	1.38	5520	36	4.16	7470	27	1.96	13 100	15	2.49	15 700	13
11	Pyridine	5.19	1.46	2620	76	3.96	6590	30	0.52	6850	29	0.78	7580	26
12	<i>N,N</i> -Dimethylaniline	5.15	2.88	5490	36	8.75	8420	24	3.85	15 700	13	5.04	18 800	11
13	2,6-Lutidine	6.99	4.85	4340	46	6.48	6860	29	1.08	8730	23	1.06	9430	21
14	3,4-Lutidine	6.77	7.62	3720	54	10.4	7130	28	1.70	9810	20	1.91	10 300	19

^a Flow: 0.4 ml/min, $T=25^\circ C$, UV (254 nm), column **IV**, pH 5.5: water–acetonitrile–acetic acid– NEt_3 (70:30:0.28:0.48); pH 8.2: water–acetonitrile–acetic acid– NEt_3 (70:30:0.25:0.60). column **III**, pH 5.3: water–acetonitrile–acetic acid– NEt_3 (98:2:0.25:0.5); pH 8.4: water–acetonitrile–acetic acid– NEt_3 (98:2:0.24:0.60).

Table 4

Comparison of data obtained from the separation of compounds **15–18** on poly-NBE (column **II**) poly-ONDCA (column **III**) and poly-NBE-*co*-ONDCA (column **IV**) grafted silica^a

No.	Compound	Column IV			Column III			Column II		
		<i>k</i>	<i>N</i> (1/m)	<i>h</i>	<i>k</i>	<i>N</i> (1/m)	<i>h</i>	<i>k</i>	<i>N</i> (1/m)	<i>h</i>
15	6-Hydroxyquinoline	1.30	7420	27	2.25	7860	25	0.51	5350	37
16	8-Hydroxyquinoline	1.73	8130	25	3.24	8110	25	0.72	6250	32
17	4-Hydroxyquinoline	4.03	10 600	19	3.01	8110	25	3.43	5570	36
18	2-Hydroxyquinoline	10.2	16 000	12	4.21	8030	25	13.5	8270	24

^a Conditions: mobile phase water; 8% acetonitrile, 20 mM tartaric acid (pH 2.4). Flow: 0.4 ml/min. Injection volume: 5 μ l (5 ppm each). UV (254 nm). Temperature: 25°C. Elution order: compounds **15**, **16**, **17**, **18**.

separations of isomeric basic analytes that are highly soluble both in water and organic solvents and are similar in terms of structure and pK_a . The general applicability of this concept is demonstrated by the separation of four isomeric hydroxyquinolines (Table 4). Under isocratic conditions, optimum separation is achieved at pH 2.4. The resulting values for *h* are within a range of 12–27. Again, the separation behavior of the mixed column (column **IV**) was better than on a pure RP or ion-exchange column.

An important feature, that finally needs to be addressed, is the chemical stability of a column. Both coated and grafted pure NBE-based supports exhibit a comparably high tendency towards oxidation due to the high reactivity of poly-NBE. Nevertheless, poly-ONDCA- and poly-NBE-*co*-ONDCA-coated supports used in this contribution exhibit a remarkable chemical stability ($0 < \text{pH} < 12$) even over years [19,27]. In contrast, poly-ONDCA- and poly-NBE-*co*-ONDCA-grafted supports may only be used within a pH range of 4–10. Nevertheless, within the given pH limits, these grafted columns also exhibit a good long-term stability. Thus, these columns appear to be stable over at least 6 months. Standard deviations (σ_{n-1} , $n=3$) for t_R and $w_{0.5}$ for a sample of isomeric hydroxyquinolines obtained from multiple injections were in the range of 0.1–0.3% and 0.2–0.6%, respectively.

4. Summary

Ring-opening metathesis graft-polymerization allows the design and controlled synthesis of stationary phases in terms of functionality, polarity and/or

capacity via the architecture of the homo- and block-copolymers that are attached to the surface of the carrier. This gives access to tailor-made supports and additionally permits to carry out more detailed investigations on separation mechanisms.

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