

Synthesis and studies on core-shell type anion exchange resins based on a hybrid polymeric support

Piotr Cyganowski, Dorota Jermakowicz-Bartkowiak

Division of Polymer and Carbonaceous Materials Faculty of Chemistry, Wrocław University of Technology, Wrocław, Poland

Correspondence to: P. Cyganowski (E-mail: piotr.cyganowski@pwr.edu.pl)

ABSTRACT: In pursuit for new materials for recovery of noble metals, novel anion exchangers, based on new type of core-shell polymeric supports have been synthesized. The designed matrices, with reactive chloromethyl groups concentrated on a surface of the polymeric base, the Amberlite XAD-4 adsorbent, have been modified using ethylenediamine and polyethyleneimine. The obtained ion exchangers were employed in processes of sorption of gold, platinum, and palladium chlorocomplexes, then, they were compared to similar resins based on volumetric polymeric supports. The studies covered porosity measurements, determination of sorption behavior in the presence of counter ions as well as kinetic and column studies. Ultimately, an attempt to access a core-shell character of the resins has been made using digital-optical microscopy. The proceeded analyses allowed to determine the localization of the resins' functionalities and their advantages over traditional ion exchange resins. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43841.

KEYWORDS: functionalization of polymers; separation techniques; synthesis and processing

Received 5 January 2016; accepted 26 April 2016

DOI: 10.1002/app.43841

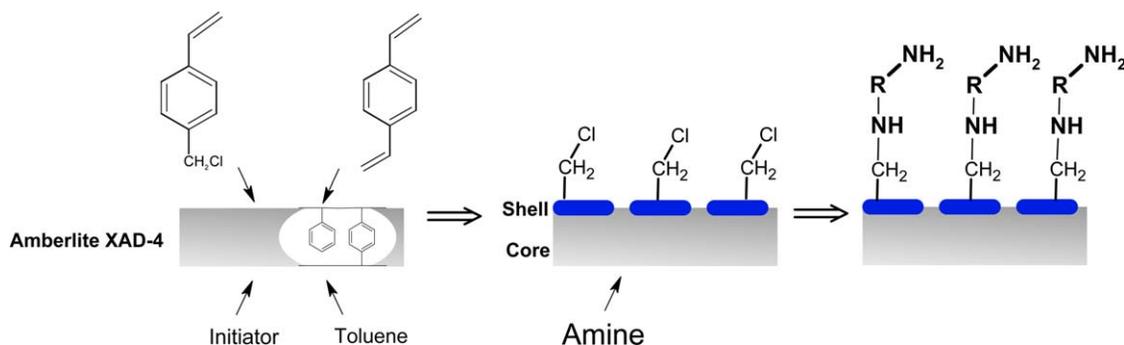
INTRODUCTION

The Environmental Program of the United Nations claims that Waste Electronic and Electrical Equipment (WEEE) is becoming a serious problem. Nowadays, human society generates enormous amounts of WEEE, which, in the face of developing technologies will constantly rise year by year.¹ Among major components of electronic scrap a great amount of metals (40%), plastics (30%), and ceramics (30%) may be distinguished.^{2,3} Within that type of wastes printed circuit boards (PCB) are recognized as the most valuable secondary source of metallic materials. They consist mainly of copper (20%), iron (8%), tin (4%), nickel (2%), lead (2%), zinc (1%), silver (0.2%), gold (0.1%) as well as palladium and platinum (0.005%).^{3,4} Some of these elements are considered as potentially harmful, other, as extremely precious and rare. For that reason, there is a pressing need for managing the *e-wastes*. Because of the fact that WEEE contain precious metals in trace or even in ultra-trace amount, an extensive use of anion-exchange resins may be found there. Functionalized resins have multiple and well-documented applications, such as waste water treatment,⁵ drugs purification,⁶ as well as metals separation.^{7,8} Traditional extraction methods are not sufficient for recovery of desired element from diluted media; therefore utilization of ion exchange resins is considered as the only economically viable way to retrieve metals that had been once used.⁹

The most popular supports for preparation of anion exchangers are copolymers of styrene (S) and divinylbenzene (DVB).¹⁰ Application of these materials requires, in first step, chloromethylation, using chloromethyl ether or bis chloromethyl ether as the alkylating reagents, and then, subsequent functionalization with a suitable reactivities in order to introduce the ion-exchange functionalities into the S/DVB copolymer.¹¹ However, a usability of the mentioned alkylating agents is strongly limited due to their strongly carcinogenic character^{12,13}; therefore there is a pressing need of developing alternative functionalized resins.

Since then Subramonian¹⁴ proposed the use of a vinylbenzyl chloride (VBC) instead of styrene as a starting monomer for functional resins' preparation, many papers on the ion-exchangers based on VBC/DVB supports, including works of the authors of the present studies, have been published.^{10,15–19}

The VBC used as a functionality may render diffusional limitation in and out the polymer matrix during the chemical reaction because the active sites (reactive chloromethyl groups) are not concentrated on the surfaces of the beads.²⁰ Furthermore, alternative methods of synthesis, involving the addition of the functional monomer (VBC) simultaneously to the supporting monomers S and DVB, leads to the possibility of this relatively expensive active-site functional monomer being occluded inside the polymer network, and, as the result, could be not available for the reaction.^{20,21} Other, more effective methods, as preparation



Scheme 1. Simplified representation of the applied synthesis procedure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of macroporous materials with large pores²² as well as surface-gradient polymerization using the VBC²¹ are not fully successful.

For that reason, in our previous work²³ we have reported the new approach of improving accessibility of the groups derived from precious VBC. Our idea is focused on limiting the amount of expensive reagents utilization, simultaneously enabling their efficient usage. For that reason we have designed a synthesis procedure, that allowed to obtain new polymer supports, based on interpenetrating polymer networks (IPN), with the reactive chloromethyl groups, derived from the VBC/DVB copolymer, concentrated on the surface of these matrices.²³ The method is a subject of a patent application sent to the Polish Patent Office and registered under number P.410196.²⁴

Those copyrighted materials may possess multiple applications due to their accessible, reactive moieties. Therefore, the aim of the present studies is synthesizing new core-shell type anion exchangers based on those polymeric matrices. Because of the fact, that no similar resins have ever been reported, within current paper we are proposing a modification procedure, that simultaneously, with further treatment, allows to access the usability of the new anion exchange resins as well as localize their functionalities revealing the core-shell character.

The best within designed polymer matrices^{23,25} have been reproduced and functionalized using ethylenediamine (EDA) and branched polyethyleneimine (PEi) in order to obtain series of new anion exchangers designed for sorption of chlorocomplexes AuCl_4^- , PtCl_6^{2-} and PdCl_4^{2-} from HCl solutions. Localization of the chloromethyl groups, and, in subsequent step, amino functionalities introduced into investigated polymeric supports has been determined using digital-optical microscopy.

The concept of the synthesis leads to the obtainment of a new anion exchange resins that, due to their nature, should not suffer diffusional limitations as their conventional equivalents. For that reason, the synthesized core-shell type resins were compared to some volumetric ones, synthesized using a set of commercial chloromethylated S/DVB copolymers donated by Purolite Co. and suspension VBC/DVB copolymer.

EXPERIMENTAL

Reagents

Monomers for the polymerization procedure have been purchased from Sigma-Aldrich Co., branch in Poznań, Poland. The VBC, 99%, (mixture of 3 and 4 isomers) and DVB, 80%, were purified

before use by distillation. A commercial base, the Amberlite XAD-4 adsorbent as well as polyvinyl alcohol (PVA, $M_w = 130,000$) were acquired in Fluka via Sigma-Aldrich Co., branch in Poznań, Poland and used as received. Ethylenediamine (EDA, 99%) and branched polyethyleneimine (PEi, $M_w = 25,000$) applied for modification processes were purchased from Sigma-Aldrich Co., branch in Poznań, Poland, and applied without any pretreatment.

Standard metals' solutions (1 g g^{-1}) have been acquired from Sigma-Aldrich Co., branch in Poznań, Poland, and further diluted to retrieve AAS calibration points. Solutions applied for studies on sorption were prepared by dissolving the $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, and diluting solutions of H_2PtCl_6 and H_2PdCl_4 in 0.1 M HCl, 1 M HCl and 3 M HCl, respectively. These acids were acquired from Avantor Performance Materials Inc., Gliwice, Poland (gold) or INNOVATOR Ltd., Gliwice, Poland (platinum and palladium).

Synthesis of the Core-Shell Type Anion Exchange Resins

The procedure of the ion exchange resins synthesis is displayed in Scheme 1. First, the commercial, macroporous polymeric adsorbent, Amberlite XAD-4, was swollen overnight in organic solvents and a mixture of monomers, VBC and DVB. Then, using a suspension polymerization technique, according to the procedure described in detail in the Ref. 23, the new core-shell type supports have been synthesized. These polymers are characterized by a specific localization of the chloromethyl functionalities, ready for modification. Finally, the as-prepared carriers were modified in course of an electrophilic substitution of chlorine (derived from the $-\text{CH}_2\text{Cl}$ groups) by amines obtaining series of the core-shell type anion-exchange resins (Scheme 1).

Details of the three-step synthesis procedure is provided below.

Impregnation and Polymerization Procedure. The procedure involves, as a 1st step, an impregnation of the Amberlite XAD-4 adsorbent. Starting monomers, VBC and DVB (10 mol % in respect to VBC), have been placed in a glass vial. Then, organic solvents, toluene (Solution A) or mixture of toluene and dodecyl alcohol (Solution B) were added in order to obtain a solution where monomers (VBC and DVB) constitute 65 wt % (resin 4P, Solution A) or 45 wt % (resin 2P, Solution B). The azobisisobutyronitrile (AIBN, 0.2 wt % in respect to monomers) was used as the initiator of polymerization.

From the thermodynamic point of view, the applied toluene is a good solvent for VBC and DVB, whereas dodecyl alcohol,

again, thermodynamically is considered as a bad one. For that reason, for the purpose of the present studies, toluene will be called a sol, while dodecyl alcohol non-sol solvent.

In general, application of the sol toluene (Solution A) results in obtainment of an expanded-gel structure of the introduced VBC/DVB copolymer (resin 4P). On the other hand, usage of the mixture of the sol toluene and non-sol dodecyl alcohol (Solution B) results in porous structure of the introduced VBC/DVB network (resin 2P).^{23,26}

The Amberlite XAD-4 adsorbent was being swollen in the appropriate mixture for 18 h at +3 °C in order to prevent initiation of the polymerization. After that, the impregnated XAD-4 resin has been separated from an excess of the organic phase in course of a centrifugation.

Then, the impregnated XAD-4 supports have been suspended in an aqueous phase composed of a mixture of poly(vinyl alcohol) (PVA) and anhydrous calcium chloride (CaCl₂). The mixtures have been stirred (300 RPM) for 21 h under reflux condenser at 55–90 °C in a tubular reactor equipped with a propeller stirrer.

The synthesized polymeric carriers have been sieved in order to receive fraction of ~0.1 cm of the resins' beads. Then, the polymers were extensively washed with acetone, cold, hot and once again cold distilled water, respectively. Next, they have been swollen in acetone, dried and extracted in toluene in order to remove all of the unreacted monomers and oligomers.

After the described procedures, the polymeric supports have been dried and used for further step of the procedure.

Modification Procedure. The new anion exchange resins based on the copyrighted 2P and 4P carriers were prepared by the method previously presented in the Ref. 15. The procedure was as follows: about 2 g of each of the synthesized polymeric matrices, 2P, 4P, were swollen overnight in 70 cm³ of DMF in 250-cm³ three-necked round bottom flasks. Next the EDA (resins 2PE, and 4PE) or PEi (resins 2PEi and 4PEi) were added. Then, the flasks were equipped with a reflux condensers and thermometers. The mixtures of the polymers and amines were refluxed for 6 h at a boiling temperature of the solvent in order to conduct an electrophilic substitution of chlorine atoms by means of nucleophilic attack of the amine to the carbon, derived from the reactive chloromethyl groups. Anion exchange resins, obtained using described method were coded using name of a polymeric matrix (2P, 4P) and letters corresponding to the amines: E for EDA and Ei for PEi. As a result a series of resins: 2PE, 2PEi, 4PE, 4PEi were obtained.

The resultant products were filtered and washed successively with cold, hot, and again cold water until the pH of the eluent was neutral. Then, the ion exchange resins were placed in glass ion exchange columns. 1 M HCl, distilled water, 1 M NaOH, distilled water, and 1 M HCl were passed through, respectively, until the outflow reached neutral pH. Next, the polymers were washed with 0.1 M HCl, 0.001 M HCl, and used for sorption studies.

Sorption of Noble Metals

Ability of the synthesized ion exchangers for sorption of AuCl₄⁻, PtCl₆²⁻, and PdCl₄⁻ was evaluated using multicomponent solu-

tions in 0.1 M, 1 M, and 3 M HCl (where each metal was present in the amount of 0.24 mM). Such a concentration allowed for an assessment of the resins' ability to remove adsorbates from diluted systems close to these that are being utilized on an industrial scale.⁴ The sorption processes were proceeded using batch method in accordance to the procedure previously presented in Ref. 27, where resins (0.05 g) were being shaken with a specific solution (20 cm³) for 48 h at ambient temperature. Next, the polymers were separated by filtration.

Influence of Competitive Ions

Resins' sorption behavior in the presence of competitive ions that in reality are present in solutions prepared using aqua regia was assessed using solution of gold, as metal that reveals stable species distribution.²⁸ The procedure of the experiment was the same as described above. Difference was that the investigated resins were being shaken with solution of Au(III) (0.72 mM) in 0.1 M HCl where simultaneously sodium chloride and sodium nitrate (as chloride-nitrate ions generators) were introduced. The competitive ions' concentration was set at 1 g dm⁻³ in order to ensure their excess toward gold. The amount of Au(III) in the solution was adjusted to 0.72 mM to retain the same ratio of anion exchange functionalities to the metal's species as during studies on tri component solution of Au, Pt, and Pd.

Kinetic Studies

A core-shell character of the investigated resins may significantly affect sorption kinetics. In order to enable a possibility of appliance of kinetic models, the influence of contact time on sorption was investigated in single component Au(III) systems in 0.1 M HCl, where gold was present in amount of 0.24 mM.

The resins 2PE, 2PEi, 4PE, and 4PEi in a swollen form (about 0.05 g) were introduced into 25 cm³ bottles. Then, 20 cm³ of the Au(III) solution was added. Amount of the resins as well as volume of the solution created a possibility of entire removal of gold accessing a suitability of the resins from practical point of view. The core-shell type anion exchange polymers were then being contacted with the solution for 2, 5, 8, 16, and 24 h, respectively. After a time that has been set, the ion exchangers were quickly separated by filtration, final concentration of Au(III) in a remaining solution was measured and sorption (mg g⁻¹) was calculated.

The same procedure has been also applied for the resin E4 previously presented in the Ref. 27 (EDA-modified VBC/DVB support, Table IV). That allowed to reveal a difference between regular, volumetric materials, and the new, core-shell type ones.

The received experimental data were matched with Lagergren's, pseudo first order (PFO), and Ho's, pseudo second order (PSO) mathematical models, respectively. Kinetic parameters were calculated using reduced form of Lagergren's¹ equation,^{29,30} and Ho's² equation as well³¹:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{t} \cdot t \quad (1)$$

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \cdot t \quad (2)$$

where t (min) is time, q_e (mg g⁻¹) is sorption at equilibrium, q_t (mg g⁻¹) is sorption in time t . Parameter k_1 (min⁻¹) was

calculated from slope of $\log(q_e - q_t)$ versus t plot. Parameter k_2 ($\text{g mmol}^{-1} \text{min}^{-1}$) was obtained from intercept of t/q_e against t plot.³²

Column Studies

For the purpose of dynamic sorption and desorption tests, a small PE column has been used. Into the 5-cm³ column the swollen resin 2PE was introduced (1.88 g). Dimensions of the resin's bead were measured as 3.7 cm height and 1.0 cm diameter. Then, tri-component solution of Au(III), Pt(IV), and Pd(II) (0.24 mM of each metal) in 0.1 M HCl was added through the resin's bead at $10 \times 10^{-6} \text{ dm}^3 \text{ s}^{-1}$ flow rate within 72 h. Such a conditions allowed to pass 2.5 dm³ of metals' solution. The column effluent was collected in 15 cm³ portions using a fraction collector. Then, the concentrations of the Au(III), Pt(IV), and Pd(II) were determined.

After the described procedure, the resin's bead has been relaxed in the course of countercurrent washing using distilled water.

Finally, in respect to the procedure previously described in Ref. 15 the resin 2PE was regenerated using 5% solution of thiourea in 0.1 M HCl. The eluent was selected due to its ability to create stable complexes with nitrogen atoms present in EDA functionalities, efficiently removing immobilized metals' chlorocomplexes.^{8,33,34} The column was washed with just a 150 cm³ of the eluent applying $10 \times 10^{-6} \text{ dm}^3 \text{ s}^{-1}$ flow rate. The species that have been being desorbed were collected in 5 cm³ fractions and a concentration of each metal was determined.

Analysis Methods

The 0.001 M HCl regain was measured using centrifugation technique.³⁵ The nitrogen and chlorine content were determined in accordance to the Kiejdahl's^{36,37} and Schöniger's³⁸ methods, respectively. Hecker's procedure was applied for determination of the anion exchange capacity, Z_H .³⁹ The determined characteristics of the investigated resins is presented in Table I.

The FTIR spectra in KBr pallets were recorded using Perkin-Elmer System 2000 spectrophotometer.

The concentration of the metals remaining in the solution was determined using Perkin-Elmer AAnalyst 200 atomic spectrophotometer¹⁶ set at 242.8 nm (gold), 266.0 nm (platinum), and 244.8 nm (palladium) wavelength. The device was calibrated using standard 1000 mg dm⁻³ solutions of gold, platinum, and palladium, diluted in a way to get 5 calibration points between concentration of 0 and 50 ppm of a metal. Lamp current was set at 4.0 mA for determination of Au, 10 mA for Pt, and 5 mA for Pd. The analysis was performed at width of a slit set at 0.5 nm (gold) and 0.2 nm (platinum and palladium). Flow ratio of acetylene to air was set at 1.15:10.

Removal (%) of gold, platinum, and palladium that represents the ability of the resins to concentrate the solutions as well as amount of sorption (mg g^{-1}) were calculated using mass balance.

The results of noble metals sorption from 0.1 M HCl solution using resins 2PE and 4PE were compared to those presented in Ref. 27 where ion exchange resins based on a regular EDA-

Table I. Characteristics of the Obtained Anion Exchangers

Resin	Amine	W ^a	Cl(1) ^b	Cl(2) ^c	Cl(3) ^d	N ^e	Z _H ^f
2PE	EDA	0.77	1.35	0.09	2.60	2.44	2.36
4PE		0.57	1.95	0.21	2.96	2.14	2.21
2PEi	PEi	0.54	1.35	0.25	2.28	2.12	2.01
4PEi		0.48	1.95	0.52	2.61	2.23	2.19

^a 0.001 M HCl regain [g g^{-1}].

^b Chlorine content in the resins before modification process [mmol g^{-1}].

^c Unreacted chlorine (covalently bonded) after modification process [mmol g^{-1}].

^d Total chlorine content (sum of ionic chlorine and covalently bonded chlorine) [mmol g^{-1}].

^e Nitrogen content [mmol g^{-1}].

^f Ion exchange capacity [mmol g^{-1}].

modified S/DVB and VBC/DVB copolymers were synthesized using the most effective and resource-intensive method of modification the authors' have ever developed.

The porosity of the core-shell type anion exchange resins was determined in course of N₂ adsorption at 77 K using an Autosorb IQ gas sorption analyzer (Quantachrome). The samples were previously outgassed at 60 °C for 24 h. BET equation was applied to calculate the specific surface area (S_{BET}). Total volume of the pores (V_T) was determined in course of investigation of the amount of nitrogen adsorbed at a relative pressure of $p/p_0 = 0.96$.

A morphology of the anion exchange resins was assessed using scanning electron microscope JSM 5800LV (SEM, equipped with the JSIS 300 Oxford X-ray analyzer) and NanoFocus $\mu\text{surf expert}$ confocal microscope made available courtesy of company OPTA TECH Ltd., Warsaw, Poland.

The core-shell character of the resins was confirmed using a colorimetric procedure. The application of the method was possible due to the visible change of the color of noble metals' complexes that results from their sorption on amino functionalities incorporated into synthesized resins, making them colorimetric markers. The change of the color is limited only to the areas, within the resins' structures, where the amino groups, saturated with the precious metals are placed.¹⁷ Therefore, the localization of the anion exchange functionalities was determined using digital-optical microscopy using Delta Optical Biolight, Warsaw, Poland 300 microscope.

RESULTS AND DISCUSSION

The new core-shell type supports developed in our previous work²³ were transformed into new anion exchangers and used for sorption of Au(III), Pt(IV), and Pd(II). The studies allowed to determine their usability for uptake of the noble metals as well as localization of their amino functionalities.

Modification

Table I displays value of chlorine content present in the used polymer matrices [Cl(1), 2P, 4P] before modification process. Values of Cl(2) and Cl(3) show unreacted chlorine and total one, respectively. The difference Cl(3) – Cl(2) determine ionic chlorine, that find its source in the ability of amino groups to

protonate in hydrochloric solutions.³⁸ The difference $\text{Cl}(1) - \text{Cl}(2)$ delivers the value of the substituted chlorine amount indicating modification efficiency.

The modification process was the most efficient in case of the anion exchange resins modified using EDA (2PE, 4PE), where almost all of the chlorine in the initial matrixes was replaced by the amino functionalities. The least effective process has been found in case of the resin 4PEi, where 73% of initial chlorine was displaced. As far as the modification procedure was the same for all of the anion exchangers, the source of that phenomenon may be found in the composition of the solutions used for impregnation of the XAD-4 adsorbent. The Solution A (resin 4P) consisted of 65 wt % of the monomers (VBC, DVB) while Solution B (resin 2P) consisted of 45 wt % of the monomers.²³ It is possible that richer mixture of the monomers (Solution A) could cause reduction of space available within the 4P matrix simultaneously decreasing the accessibility to the chloromethyl groups regardless to the architecture of the porous structure. The conclusion seems to be supported by lower 0.001 M HCl regain (W) of the anion exchangers based on the 4P support (Table I).

Lower uptake of the acid as well as crosslinked structure of the initial polymeric base (XAD-4) indicate that the transport of a medium (acid or in next step, adsorbates) will be limited due to the poorer porous structure of the resin 4P. At the same time, the resins based on the support 2P is being swollen to the greater extent (Table I), which means that its polymeric network acts a better transportation role reflecting with more accessible functional groups.

In consequence, despite the greatest chlorine content (1.95 mmol g^{-1} , Table I²³), the resin 4P turned out to be less efficient during modification than its equivalent (resin 2P) obtained using poorer monomers' mixture as well as sol and non-sol solvents. The effect is followed by the ion exchange capacity value (Table I, Z_H , resins 2PE and 4PE): even though the resin 4PE reveal greater total chlorine content, the determined ion exchange capacity (2.21 mmol g^{-1}) is slightly lower than the one determined for the resin 2PE (2.36 mmol g^{-1}).

In general, unreacted chlorine content [$\text{Cl}(2)$, Table I] is greater for the resins based on the polymeric support 4P (obtained using richer monomers' solution and only the sol toluene). However, the evaluation of modification effectiveness is a complex issue and may be also correlated with type of the amines used for the modification. Method of functionalization using PEi (resins 2PEi and 4PEi) leaves significant amount of unreacted chlorine behind (Table I). The effect is probably associated with branched structure of the PEi in which single particle is much larger than EDA; therefore, its access to the chloromethyl groups could be difficult despite core-shell nature of the polymeric supports.

The amount of chlorine, substituted by PEi [$\text{Cl}(1) - \text{Cl}(2)$, Table I], in comparison to the nitrogen content (N, 2PEi, 4PEi, Table I) indicates that each of the waning chlorine atoms corresponds to the 2–3 of introduced nitrogen atoms. Taking into account the branched structure of the PEi, there is a possibility

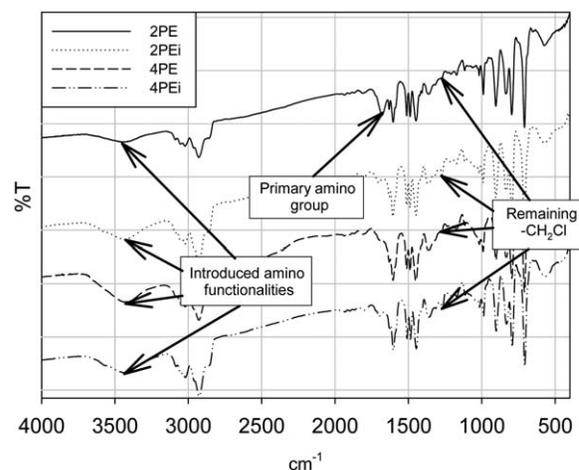


Figure 1. Recorded FTIR spectra for resins 2PE, 2PEi, 4PE, and 4PEi.

that nitrogen atoms within a single PEi molecule may participate in substitution of more than one chlorine atom. This means that matrices 2P and 4P could be additionally crosslinked during modification process. The phenomenon may explain the lower ion exchange capacity (Z_H , Table I) as well as 0.001 M HCl regain value (W , Table I) compared to their equivalents synthesized using EDA. In general, the data (Table I) indicate that the best efficiency of modification is achieved for the matrices obtained using poorer monomers mixture and solvents being sol and non-sol toward them²³ as well as the amines characterized by relatively small particles (EDA).

Analysis of the FTIR Spectra

During previous research cited in Ref. 23, the FTIR spectra recorded for the equivalents of the resins 2P and 4P revealed strong peaks responsible for the interactions between chlorine and carbon in the chloromethyl groups. That bands almost disappeared during present studies after modification process (Figure 1) and the new ones at 3444 cm^{-1} (resin 2PE), 3441 cm^{-1} (resin 2PEi), 3433 cm^{-1} (resin 4PE), and 3437 cm^{-1} (resin 4PE) appeared. Those peaks have been recognized as the ones, responsible for the presence of $-\text{NH}$ groups suggesting that the modification procedure completed successfully.

However, the recorded FTIR spectra, displayed in Figure 1, reveal very weak bands at 1273 cm^{-1} (resin 2PE), 1269 cm^{-1} (resin 2PEi), 1271 cm^{-1} (resin 4PE), and 1267 cm^{-1} (resin 4PEi) responsible for the C–H interactions, where simultaneously chlorine is attached to the carbon. Those bands confirm that not all of the reactive chloromethyl groups reacted with the amino moieties used for functionalization of the resins 2P and 4P (Table I, Figure 1).

The sharp peak at 1680 cm^{-1} (2PE, Figure 1) corresponds to the vibrations of the primary amino groups $-\text{NH}_2$, derived from EDA.¹⁵ Similar bands are not being observed in case of the resins 2PEi, 4PE, and 4PEi (Figure 1). As far, as PEi-modified resins should not possess those functionalities, it was expected that resin 4PE (where EDA was introduced into) should possess $-\text{NH}_2$ groups. Absence of these indicate that additional crosslinking of the polymer matrix due to bisamine functionality have occurred. The phenomenon is also

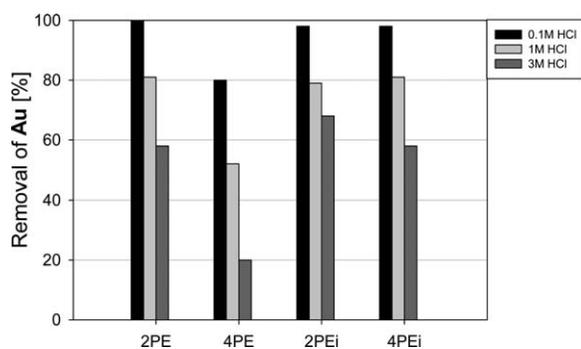


Figure 2. Removal of gold from tricomponent (Au, Pt, Pd) solutions in 0.1, 1, and 3 M HCl.

accompanied by the lower 0.001 M HCl regain of the resin 4PE compared to the resin 2PE (Table I); therefore it is expected that the anion-exchange resins based on the 4P support will probably reveal smaller sorption capacity than their equivalents based on the matrix 2P.

Sorption Studies

Figures 2–4 display calculated percent values of the Au(III), Pt(IV), and Pd(II) removal from tricomponent solutions in 0.1 M, 1 M, and 3 M HCl, respectively.

Equivalent molar ratio of the metals' concentration (0.24 mM) allowed for direct comparison of their concentration efficiency; therefore it could be stated that sorption of all metals is the most efficient during processes proceeded from solution in 0.1 M HCl (Figure 2).

The resins 2PEi and 4PEi reveal the greatest ability to remove chlorocomplexes of the metals irrespective of concentration of the acid. The nitrogen content (Table I) determined for these resins suggests that they should reveal slightly lower sorption of the noble metals than their EDA-modified equivalents (resins 2PE and 4PE). Nitrogen content presented in the Table I is expressed in reference to 1 g of the resin. Furthermore, the procedure of its analysis (introduced by Kjeldahl³⁶) ignores issues with accessibility determining whole volume of a sample. Introduction of the branched PEi, that molar mass is much greater comparing to EDA, could effectively increase the mass of the beads of the resins causing that the same mass of the resins 2PEi and 4PEi might contain fewer nitrogens than resins 2PE

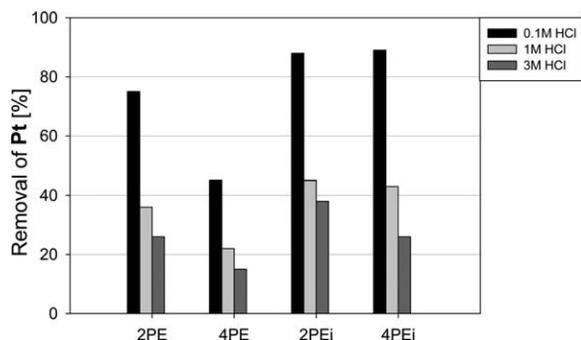


Figure 3. Removal of platinum from tricomponent (Au, Pt, Pd) solutions in 0.1, 1, and 3 M HCl.

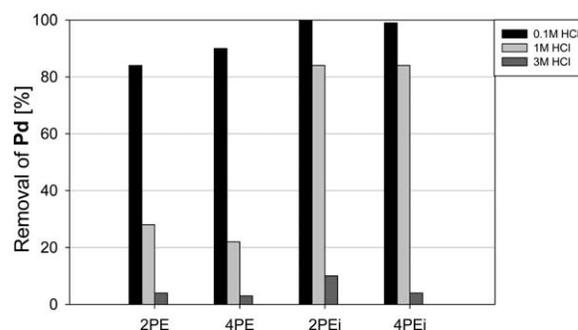


Figure 4. Removal of palladium from tricomponent (Au, Pt, Pd) solutions in 0.1, 1, and 3 M HCl.

and 4PE. For that reason, a different explanation should be found.

The phenomenon could be explained by “soft and hard acids and bases theory.”⁴⁰ PEi groups, with multiple nitrogen donor atoms, that have been incorporated into structures of the resins 2PEi and 4PEi may act as “soft base”; therefore it could remove Au(III), Pt(IV), and Pd(II), considered as “soft acids”, with much greater efficiency than regular ion-exchange. On the other hand, the EDA functionalities introduced into supports 2P and 4P (the resins 2PE and 4PE, respectively) could also coordinate chlorocomplexes of the metals, but, taking into account branched structure of the PEi, the effect could be much more intensive.¹⁵

Sorption of Pd(II) that proceeds with great efficiency from solutions in 0.1 M and 1 M HCl (Figure 2) decreases significantly during loading from solution in 3 M HCl (Figure 4). According to Hubicki *et al.*,⁴¹ palladium species distribution differs with changing pH (chloride concentration) of the solution. In range of pH 1.0–2.0 palladium exist in forms PdCl_4^{2-} , $\text{PdCl}_2(\text{H}_2\text{O})_2$ and $\text{PdCl}_3(\text{H}_2\text{O})^-$. Furthermore, at 3 M HCl, HCl_2^- anion becomes competitive toward PdCl_4^{2-} complex.

Regardless to the sorption of Pd(II) behavior, removal of all of the metals by all of the resins decreases with decreasing pH (increasing concentration of the HCl). Cause of the effect may have multiple sources, but the most probably one is the fact that the more acidic solution is the more tightened polymeric matrix becomes, reflecting on capturing the metals' species.¹⁰

The sorption from solution in 0.1 M and 1 M HCl, that is probably not affected by palladium chlorocomplexes distribution (the predominant species in that conditions is PdCl_4^{2-}), reveal that platinum is removed with the least efficiency.

The effect is probably attributed to the fact that in solvent extraction processes, flat and rectangular complexes AuCl_4^- and PdCl_4^{2-} are more competitive toward octahedral platinum complex PtCl_6^{2-} .⁴² In effect, the Au(III) and Pd(II) chlorocomplexes are more competitive toward Pt(IV) resulting in decreasing sorption of platinum.

However, considerations of the sorption efficiency require taking a closer look at values of the uptake of each metal expressed in mg g^{-1} (Table II). The greatest total sorption (mg g^{-1}) capacity may be observed for the resins 2PE (68 mg g^{-1}) and

Table II. Maximum Sorption (mg g^{-1}) of the Noble Metals Registered for the Resins 2PE, 4PE, 2PEi, and 4PEi

Resin	Sorption (mg g^{-1}) ^a		
	Au	Pt	Pd
2PE	31.0	23.0	14.0
4PE	26.4	14.7	16.0
2PEi	28.6	25.4	15.6
4PEi	27.4	24.7	14.9

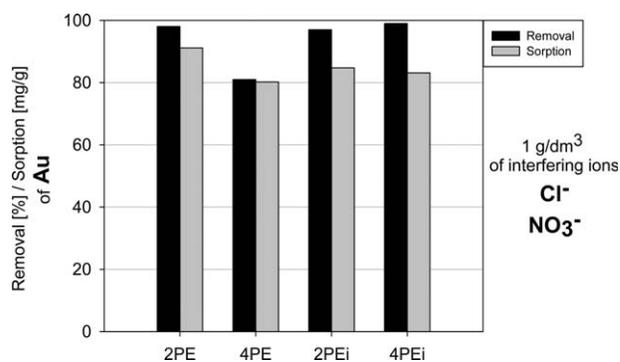
^aFrom tricomponent 0.24 mM solution in 0.1 M HCl

2PEi (70 mg g^{-1}). In general, gold was sorbed with the greatest efficiency among all of the metals. Its sorption reached 31 mg g^{-1} in case of the resin 2PE (Table II). Despite decreasing efficiency of platinum removal (Figures 2–4), its loading (mg g^{-1}) is still satisfactory. What was possible to predict, the amount of the metals' sorption is dependent on the organic solvents applied for the synthesis of polymeric support. The uptake of gold, platinum, and palladium in most cases is greater on the resins with the VBC/DVB copolymer obtained in the presence of the sol toluene and non-sol dodecyl alcohol (resins based on the support 2P). The greatest difference may be observed in case of the platinum sorption on the resins 2PE and 4PE (23 versus 14.7 mg g^{-1}) which could mean that octahedral platinum chlorocomplex suffers diffusional limitations in expanded-gel structure of the resin 4PE. A sorption of the same species on the resins modified using PEi (2PEi and 4PEi, Table II) also differs, but to lesser extent.

As expected, in accordance to the ion-exchange capacity (Table I), the resin 2PE revealed greater removal efficiency than the resin 4PE. Similar conclusion cannot be made in case of the resins modified with PEi (2PEi, 4PEi). As far as there is a possibility that chelation is employed for the discussed process, the additional crosslinking of the polymer matrix as good as the 3-dimensional structures of the functionalities become also relevant.⁴³ For that reason, the direct comparison of those two resins is complicated. Nevertheless, all of the obtained ion exchangers are suitable for concentrating the solutions of Au(III), Pd(II), and Pt(IV) in 0.1 M HCl (Figures 2–4).

Sorption in the Presence of Counter Ions

The resins were also investigated in a system where interfering ions were present (chloride and nitrate). Figure 5 displays the removal efficiency (%) and the value of sorption (mg g^{-1}) registered for the resins 2PE, 4PE, 2PEi, and 4PEi operating in Au(III) (0.72 mM) and sodium chloride–sodium nitrate solution (1 g dm^{-3}) in 0.1 M HCl. As can be seen, addition of competitive ions to the solution hardly influenced the removal efficiency (Figure 2 versus Figure 5) which still is close to 100%. The value of sorption is even greater ($80\text{--}91 \text{ mg Au g}^{-1}$, Figure 5) compared to the summarized results for the multicomponent Au, Pt, and Pd solution ($57\text{--}68 \text{ mg g}^{-1}$). The effect is caused by the fact that the Au(III) in form of AuCl_4^- is usually most easily extracted among other noble metals,¹⁵ which results directly from very stable Au(III) species distribution.²⁸ On the other hand, AuCl_4^- possess a single, negative charge,

**Figure 5.** Removal (%) and sorption (mg g^{-1}) of gold from solution of Au(III) in 0.1 M HCl with addition of 1 g dm^{-3} of chloride-nitrate ions.

which means that it occupies one “ion exchange center,” while chlorocomplexes of platinum, PtCl_6^{2-} and palladium PdCl_4^{2-} require more than one ligand to be exchanged. As a result, more functional groups are available for the Au(III). For that reason, despite the same ratio of functional groups to the metal, sorption of gold is just greater. Nevertheless, based on the results (Figure 5) it may be concluded that the investigated resins reveal a potential to be effective and selective in real systems based on aqua regia.

Sorption versus Porous Structure

The synthesized and investigated core–shell type anion exchange resins were evaluated using the procedure of low temperature nitrogen sorption and desorption. Table III displays selected parameters of the porous structures of the initial polymeric matrix Amberlite XAD-4 as well as the polymers 2PE, 4PE, 2PEi, and 4PEi.

As in our previous studies cited in the Refs. 23 and 25, an initial standard surface area as well as total volume of the pores (S_{BET} , Table III) of the Amberlite XAD-4 adsorbent decreased about 20–40% as a result of polymerization of VBC and DVB inside its matrix. Simultaneously, average size of the pores decreased not so much, therefore, it can be concluded, as it had been done before,^{23,37} that the introduced VBC/DVB copolymer probably covered internal surface area, leaving most of the pores not obstructed.

Based on the determined standard surface areas (S_{BET} , Table III) it can be clearly seen that there is a dependence between

Table III. Data of the Porous Structure Determined for the Initial XAD-4 Matrix and the Anion Exchange Resins Derived from Supports 2P and 4P

Sample ^a	BET ^b ($\text{m}^2 \text{ g}^{-1}$)	Pore volume ($\text{cm}^3 \text{ g}^{-1}$)	Average pore size (nm)
XAD-4	825	0.91	4.41
2PE	677	0.71	4.24
4PE	586	0.61	4.01
2PEi	564	0.54	4.21
4PEi	500	0.50	4.10

^aSupport 2P: mesoporous structure; support 4P: expanded-gel structure.

^bBET: Brauner–Emmet–Teller surface area.

removal/sorption efficiency of the investigated materials and their porous characteristics. In general, the resins based on the support 2P, obtained using mixture of the sol and non-solvents reveal more developed internal architecture. That phenomenon positively affected the efficiency of the resins 2PE and 2PEi, in which maximum sorption capacity of Au, Pt, and Pd is greater than in the case of their equivalents based on the support 4P (Table II). Moreover, comparing the resins 2PE with 2PEi and 4PE with 4PEi it is noticeable that the polymers modified using PEi reveal smaller BET surface area as well as total volume of the pores. That phenomenon stands together with the observed 0.001 M HCl regain presented in the Table I. Because the compared resins are based on the same polymeric support (2P or 4P) the attention should be driven to the introduced functionalities (derived from PEi). The analysis of the porous structure seems to confirm the stated above conclusion that polyethyleneimine has additionally crosslinked the polymeric supports to a greater extent than ethylenediamine. Additional amine binding reflected on smaller 0.001 M HCl regain, lower nitrogen content, less developed porosity, and finally smaller ion exchange capacity (Tables I and III).

An Assessment of the Core–Shell Type Anion Exchange Resins Morphology

Taking into account the nature of the suspension polymerization technique, there was a risk, that the introduced into XAD-4 matrix VBC and DVB monomers may had been polymerized outside the polymer beads, creating separate phase, attached to the starting support (XAD-4).

For that reason, we have subjected the synthesized anion exchange resins to a SEM/EDX analysis in order to define their morphology and average composition. The micrographs displayed in Figure 6 display the resin 2PE as a representative sample. As can be seen in the Figure 6(a) the structure of the polymeric beads is uniform. The VBC/DVB copolymer has not polymerized outside the matrix of the Amberlite XAD-4 which means that the reactive chlorine derived from the chloromethyl groups was indeed introduced in the initial polymeric base.

To estimate a localization of a specific moiety, a single core–shell type 2PE resin's pearl has been deliberately crushed and analyzed using X-ray analyzer obtaining a suitable spectrum. In Figure 6(b), a SEM/EDX micrograph has been displayed. The investigated points [EDS spots, Figure 6(b)] were selected in a way that ensure covering whole profile of the sphere. The results are detailed in Figure 6. At the first sight it can be stated that nitrogen content (wt %) increases with increasing distance from the center of the resin's bead [Figure 6(b)]. Because the synthesized resins were obtained in course of amines' introduction it clearly indicates that most of the ion exchange functionalities are concentrated on the outside part of the resin's grain, revealing gradation of the ligands. Oxygen content revealed during the studies suggests that the chloromethyl groups that were being introduced during synthesis of the support 2P partially hydrolyzed.¹⁴ According to Subramonian,¹⁴ the effect is very difficult to control and finally results with decreased number of the functionalities.

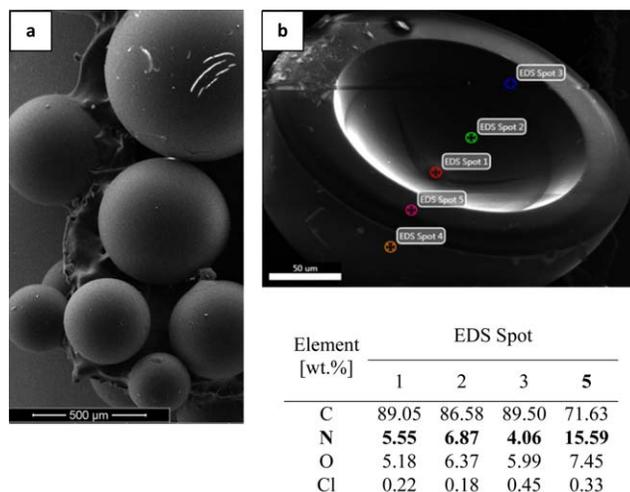


Figure 6. SEM/EDX micrographs captured for the resin 2PE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

What is interesting is minor amounts of unreacted chlorine are present in the whole volume of the polymer. However, because of the nature of synthesis (electrophilic substitution of chlorine by amines) it may be concluded, based on the amount of nitrogen, that most of the chloromethyl groups of the core–shell type support were concentrated outside the grain. The analysis confirms that the designed synthesis procedure was successful and some kind of “core” as well as “shell” may be distinguished.

The topography of the resins' 2PE and 4PE surface was assessed using *NanoFocus μsurf expert confocal microscope*. The equipment allowed to receive high-resolution 3D images of the anion exchange resins' surface, exposing structural defects and analyzing them. The size of the studied area (300 μm × 300 μm) represents the 1/3 of the surface of the resins' beads, therefore it may be considered as representative. The main advantage of the analysis is its non-invasive character.

Figure 7 displays 3D-topography maps of the Au(III), Pt(IV), and Pd(II)-saturated resins 2PE [Figure 7(a)] and 4PE [Figure 7(b)]. The differences in colors (between green and red) indicate the diversity of the investigated surface.

The analysis confirms that the resins 2PE and 4PE reveal diversified but uniform surface (Figure 7). There are some defects on the investigated samples that were probably created during processing of the resins. Long scratches indicate that high rotation of the stirrer (300 RPM)²⁵ applied during polymerization procedure might damage the polymers' grain (Figure 7).

The surface of the resin 4PE seems to be more diversified compared to the resin 2PE. The differences in the topography may be attributed to the composition of the impregnating solutions applied for the synthesis of both of the resins. More concentrated one (used to obtain the support 4P) could result with local compaction of the VBC/DVB copolymer. That observation could visualize why application of the *sol* toluene (that creates expanded-gel structure of the VBC/DVB copolymer) reflects on the less developed porosity of the anion exchange resins based on the support 4P (4PE and 4PEi).

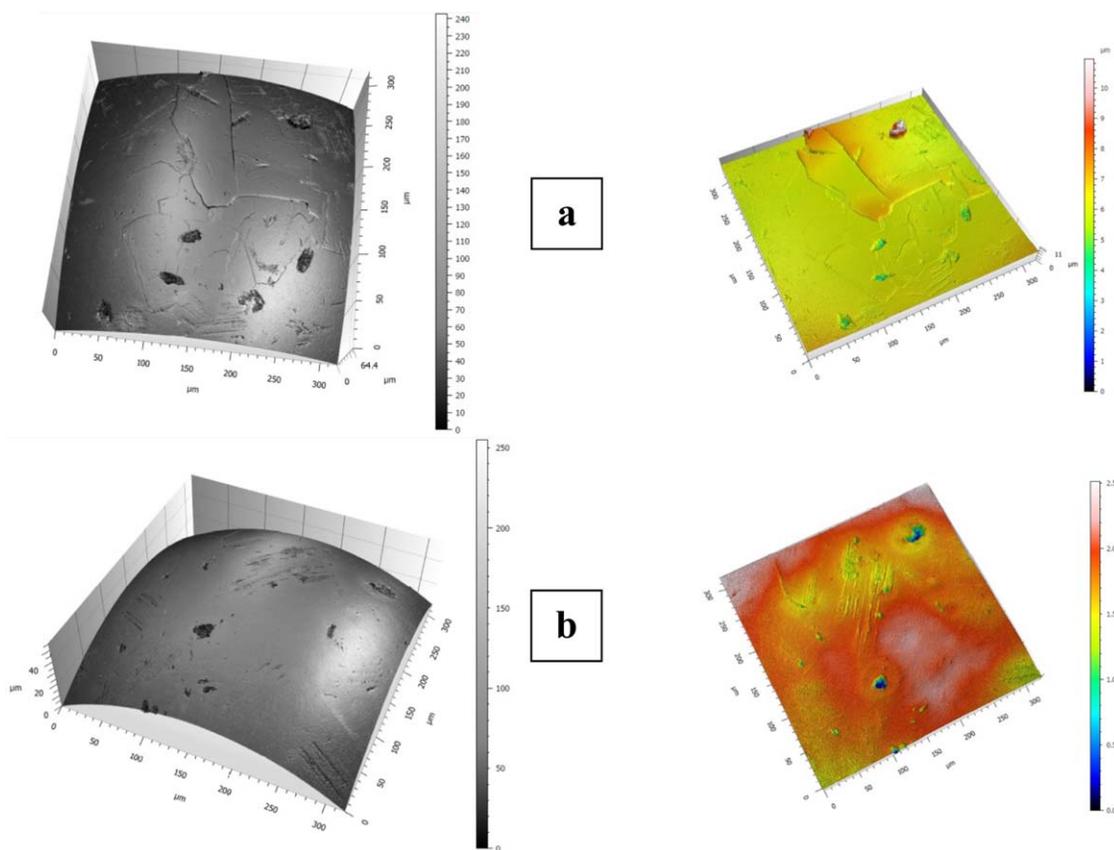


Figure 7. Analysis of the 3D topography of the resins (a) 2PE and (b) 4PE after sorption from tricomponent solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Dynamic Sorption and Desorption

The swollen resin 2PE in amount of 1.88 g (2.9 cm^3) was introduced into small 5 cm^3 column and 2.5 dm^3 of the solution containing 0.24 mM of Au(III), Pt(IV), and Pd(II) was passed through anion exchange polymer bead. The maximum dynamic sorption capacity was determined as $91.2 \text{ mg Au g}^{-1}$, $44.2 \text{ mg Pt g}^{-1}$, and $61.8 \text{ mg Pd g}^{-1}$. The results are much greater than the test proceeded using batch method (Table II). That phenomenon is simply caused by the amount of the solution which the samples were contacted with. During static sorption 0.05 g of a resin was saturated using 20 cm^3 of a medium, while column studies used 2500 cm^3 of the tri-component solution per 1.88 g of the 2PE resin.

However, the tests revealed one interesting fact. Let's take into account maximum sorption capacity expressed in mmol g^{-1} (1.27 mmol g^{-1} , calculated from molar masses of Au, Pt, and Pd). That value, after considering valency of the PtCl_6^{2-} and PdCl_4^{2-} states the amount of the occupied functional groups (2.08 mmol g^{-1}). Now, compare it to a number of EDA ligands in the introduced amount of the resin 2PE (2.29 mmol g^{-1} , based on dividing nitrogen content per amount of nitrogen atoms in EDA). It turns out that during dynamic sorption tests, where great excess of diluted metals' solution is passed through the column, almost all of the resin's 2PE functionalities (91%) are being exploited, revealing a great advantage of its core-shell character. Now, all further considerations will be referred to vol-

ume of the introduced polymer's bead (VBs for sorption, VBd for desorption).

Figure 8 gives breakthrough curves obtained during tests on dynamic sorption of Au, Pt, and Pd on the resin 2PE. At the first sight it can be said that the AuCl_4^- and PdCl_4^{2-} are being held on the column much longer than the PtCl_6^{2-} chlorocomplex. That fact proves the stated above conclusion, that the flat

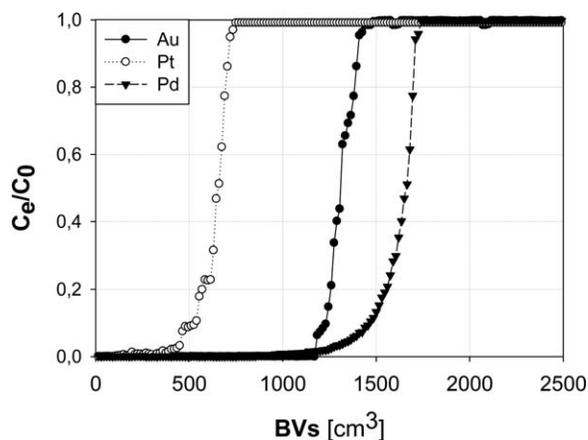


Figure 8. Breakthrough curves received during column studies on sorption of Au, Pt, and Pd from multicomponent 0.24 mM solution in 0.1 M HCl on the resin 2PE.

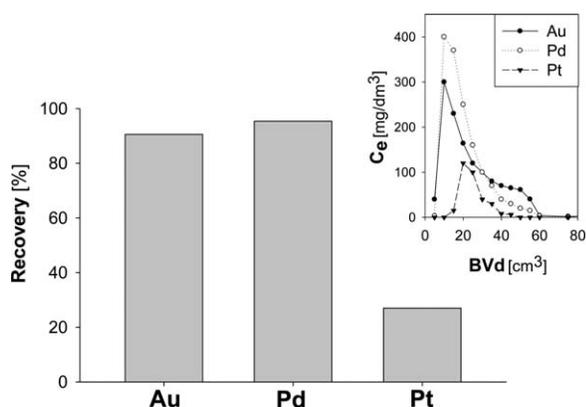


Figure 9. Dynamic desorption efficiency of Au, Pt, and Pd for the resin 2PE. Desorbing agent: 5% thiourea in 0.1 M HCl.

and rectangular Au(III) and Pd(II) species are being removed more easily. The phenomenon resulted with much lower sorption (mg g^{-1}) of platinum ($44.2 \text{ mg Pt g}^{-1}$) compared to the values registered for gold ($91.2 \text{ mg Au g}^{-1}$) and palladium (61.8 mg g^{-1}). In fact, based on the removal of platinum and palladium during batch tests (Figures 3 and 4) it was expected that Pt(IV) will be sorbed with lower efficiency. However, the differences turned out to be serious, especially taking into account molar masses of the both metals (Pd: 106 g mol^{-1} , Pt: 195 g mol^{-1}). Based on that and observing breakthrough of the column for platinum [500 cm^3 BVs, Figure 8(a)] it can be concluded that the resin 2PE reveal much greater affinity toward gold and palladium than the PtCl_6^{2-} . The phenomenon is probably induced by high crosslinkage that initial XAD-4 matrix (base of the investigated anion exchangers) is characterized by^{23,25} leading to diffusional limitations of Pt(IV) species.

During our previous studies on dynamic sorption using piperazine functionalized VBC/DVB copolymer¹⁵ platinum was removed with great amounts (over 280 mg Pt g^{-1}). However, the process was very slow, and we had not reached breakthrough or equilibrium even after 2500 cm^3 solution passed. The new anion-exchange resin 2PE despite lower efficiency of platinum sorption (Figure 8) at least swiftly passed that metal, leaving rest of its functionalities available for gold and palladium.

The noble metals-saturated polymer 2PE has been regenerated using 5% thiourea solution in 0.1 M HCl. In Figure 9 yield of

desorption is displayed. Gold was recovered in 91% and palladium in 95%. Only 27% of platinum was restored (Figure 9). The same phenomenon was observed during our previous studies,¹⁵ indicating that Pt(IV) species are very resistant for elution. Nevertheless, the degree of the Au(III) and Pd(II) recovery is satisfactory enough.

The New Core–Shell Type Anion Exchange Resins against Their Volumetric Equivalents

The tested ion exchange resins 2PE and 4PE were compared to those obtained using regular volumetric chloromethylated S/DVB and VBC/DVB copolymers, and the most efficient method of modification described in detail in Ref. 27. Both sorption tests, present, as well as those presented in Ref. 27 were proceeded applying the same conditions and the same starting solution; therefore a direct comparison was possible.

Table IV displays the data essential for discussing the differences between proceeded sorption studies using new core–shell type resins and regular, volumetric ones.

The core–shell ion exchangers 2PE and 4PE revealed approximately 60% lower sorption (S, batch studies) of the noble metals capacity than these based on S/DVB and VBC/DVB matrixes. The effect was predicted due to the character of the resins 2PE and 4PE. It was expected that the resins synthesized during present studies will be not as efficient as their volumetric equivalents, especially taking into account a specific localization of the amino functionalities. However, the core–shell type anion exchange polymers revealed a serious advantage. Nitrogen content (Table IV), that demonstrates a potential number of “ion-exchange centers”, should reflect with a much greater sorption capacity of the resins E1–E4 than these synthesized in the present work. In fact, for example, great nitrogen content observed in case of the resin E4 (9.09 mmol g^{-1} , Table IV) affects loading of noble metals 1.21 mmol g^{-1} , which constitutes approximately 13% of the introduced nitrogen atoms. On the other hand, the sorption observed on the resin 4PE (0.42 mmol g^{-1}) uses almost 40% of the available ligands (calculated on the number of nitrogen atoms in EDA) during batch sorption tests and 91% during column studies. These facts suggest that the functionalities introduced in the new core–shell type resins, despite poorer sorption capacity, are exploited more efficiently, making them relatively more profitable.

Table IV. New Core–Shell Type Ion Exchange Resins against Regular ones Based on a S/DVB and VBC/DVB Copolymers

Resin	Matrix	Functionality	Solution	N ^a	S ^b	Ref.
2PE	Core-shell IPN, MP	EDA	0.24 mM (Au, Pt, Pd)	2.44	0.41	This work
4PE	Core-shell IPN, EG			2.14	0.36	
E1	S/DVB (2%), MP			7.62	1.26	27
E2	S/DVB (4%), MP			6.78	1.34	
E3	S/DVB (4%), EG			6.00	1.11	
E4	VBC/DVB (2%), EG			9.09	1.21	

^aNitrogen content [mmol g^{-1}].

^bSorption of Au(III), Pt(IV) and Pd(II) from tricomponent solution in 0.1 M HCl [mmol g^{-1}].

MP, macroporous structure, EG, expanded-gel structure.

Table V. PFO and PSO Kinetic Parameters Determined for the Resins 2PE, 4PE, and E4 during Sorption of Au(III) from 0.1 M HCl

Resin	PFO ^a		PSO ^b		t_e
	k_1	R^2	k_2	R^2	
2PE	3.77×10^{-3}	0.7794	3.46×10^{-4}	0.9946	5
4PE	6.89×10^{-5}	0.8023	1.76×10^{-4}	0.9914	8
E4 ²⁷	7.05×10^{-3}	0.8669	6.64×10^{-5}	0.9983	16

^aLagergren's, pseudo-first order kinetic model.

^bHo's, pseudo-second order kinetic model.

k_1 [min^{-1}], k_2 [$\text{g mmol}^{-1} \text{min}^{-1}$] rate constant.

t_e , time required for reaching equilibrium (h).

There is also another issue that should be considered. More efficient usage of the ion exchange ligands observed in the case of the synthesized core-shell type resins should reflect on the sorption kinetics. For that reason, sorption studies at differed contact time were proceeded. The resins 2PE and 4PE obtained during present studies as well as the resin E4 previously presented in work cited under Ref. 27 were prepared in accordance to the procedure described in kinetic studies section and saturated with 0.24 mM solution of gold in 0.1 M HCl for 2, 5, 8, 16, and 24 h, respectively. Then, the sorption expressed in mg g^{-1} was recalculated using PFO¹ and PSO² kinetic parameters.

Table V displays determined parameters of rate constants (k_1 , k_2 , respectively), correlation coefficients (R^2), and time required for reaching equilibrium (t_e). Values of R^2 are greater in case of PSO eq. (2), and are close to 1, indicating compliance with that model (Table V). That effect is usually observed in sorption processes acting onto ion exchange resins.^{41,44} The rate constant (k_2 , Table V) determined for uptake of Au(III) using the resin 2PE (3.46×10^{-4}) is greater than in the case of the resin 4PE (1.76×10^{-4}), which results with difference in time required for reaching the equilibrium (5 vs. 8 h, t_e , Table V). That phenomenon may be directly linked with the determined porosity of the resins 2PE, 4PE (Table III). More developed porous structure observed in case of the resin 2PE probably defines accessibility of its functionalities, facilitating the sorption process.

The difference in the rate constants (k_2 , Table V) between the new core-shell type anion-exchange resins, and the regular, volumetric resin E4 (EDA-modified VBC/DVB copolymer) is significant (Table V). That reflects on the time needed for reaching the equilibrium, which is over three times longer that in case of the resin 2PE (5 vs. 16 h, Table V). Of course, longer saturation time of the polymer E4 is probably attributed mainly to a greater number of ion exchange ligands.²⁷ The more functionalities are, longer time for their saturation is needed. Nevertheless, achievement of equilibrium during sorption on the resin E4 takes 16 h and only 13% of ion exchange ligands are being exploited, while 40% of functionalities placed in the structure of the resin 2PE are saturated just in 5 h, making the process quick and efficient.

Core-Shell Character

According to a definition of IUPAC⁴⁵ a core-shell polymers comprise two polymers, each in separate phase, in which one

polymer completely encapsulate the other one. Therefore, the synthesized resins that are the subject of the present studies, in terms of that conditions are not the core-shell polymers. However, taking into account the fact that reactive sites of those polymeric supports and in subsequent step anion exchangers, based on the SEM/EDX analysis, are probably concentrated only on the surface of the beads, we have found that some of their properties are similar to those, characteristic for the core-shell polymers. For that reason, in order to highlight their nature, we decided to call them a "core-shell type."²³

Because of a homogenous nature of the obtained, partially interlaced polymer networks (S/DVB + VBC/DVB) and derived from them ion exchange resins, a direct assessment of their core-shell nature using analyses such as transmission electron microscopy (TEM) were not sufficient (the results of the attempts are available on a request). There was no clear difference between S/DVB and VBC/DVB phases. The studies proceeded using X-ray analyzer attached to a scanning electron microscope (SEM) indeed indicated, that the resins' functionalities may be concentrated outside the grains of the polymers [Figure 6(b)]. However, that type of analysis (EDX) is often recognized as speculative and not sufficient enough. Therefore, we have been forced to look at the issue from a different angle.

An opportunity to determine, without doubts, localization of the amino functionalities within the beads of the resins was provided by the proceeded sorption of the noble metals itself. Nature of the ion exchange of the chlorocomplexes AuCl_4^- , PdCl_4^{2-} , and PtCl_6^{2-} acting on amino functional groups makes them a convenient colorimetric marker.

Figure 10 displays whole concept of the experiment. In Figure 10(a), the initial resin 2P is visible. Its white-transparent color changes to yellow (2nd row) as the result of modification using different amines [Figure 10(b,b')]. Anion exchangers 2PE and 2PEi, saturated with the noble metals were deliberately crushed in order to reveal their core-shell nature [Figure 10(c,c')]. As the effect of the ion-exchange on amino functionalities (3rd row), the area where they are concentrated changed its color to intensive brown or purple [Figure 10(c,c')].¹⁷

Simultaneously, a central part (core) of the displayed beads is still white, indicating, that only outer part of the grains (shell) participated in the modification, and, in next step sorption process.

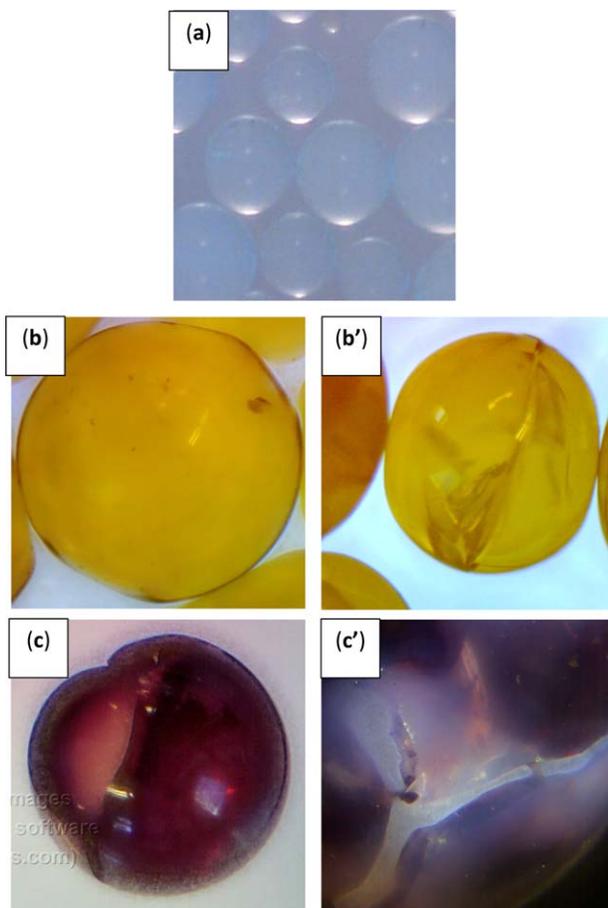


Figure 10. The micrographs of the resins (a) 2P; (b) 2PE; (b') 2PEi (c); 2PE + (Au, Pt, Pd); (c') 2PEi + (Au, Pt, Pd). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As far as the obtained resins possess clearly functionalized shell and inert core, the conclusion that they reveal a core-shell character is justified.

CONCLUSIONS

As the result of the applied synthesis procedure, the new anion exchangers with accessible functionalities, based on the new, copyrighted, core-shell type polymer supports have been obtained. Applied analyzes indicate that the investigated resins 2PE, 2PEi, 4PE, and 4PEi are suitable for removal of noble metals from their diluted solutions. The functional groups of the initial supports and synthesized from them anion exchangers are accessible. Based on the proceeded studies, the functional groups of anion exchangers derived from the supports 2P and 4P are localized on the outer side of the resins' grain creating a clear functionalized shell.

Comparing the investigated core-shell type anion exchange polymers to the resins^{15,27} based on a regular, volumetric VBC/DVB copolymer, the following observations may be made:

- Preparation of the investigated resins 2PE, 2PEi, 4PE, and 4PEi required twice less of, relatively expensive, VBC monomer (calculated per gram of the polymer).

- The chloromethyl groups of the support 2P were being efficiently transformed into ion exchange ligands of the resin 2PE. Some suitable preparations should allow to receive the same effect for the rest of the polymers.
- Despite lower sorption capacity, the functionalities of the core-shell type resins are being more effectively used and the time necessary for their satisfactory saturation is much shorter.
- The capacity of the ion exchange EDA-moieties present in the resin 2PE was efficiently exploited during dynamic sorption tests. Moreover, almost all of the gold and palladium were released from the polymer during desorption test.

ACKNOWLEDGMENTS

Authors would like to thank the OPTA TECH Ltd. for enabling the possibility of performing the confocal microscopy analysis. This work was supported by the Polish Ministry of Science and Higher Education under Grant for statutory activity of Wroclaw University of Technology.

REFERENCES

1. Burke, M. *Chem. World* **2007**, *4*, 45.
2. Zhang, S.; Forsberg, E. *Resour. Conserv. Recycle* **1997**, *21*, 247.
3. Wenzhi, H.; Guangming, L.; Xingfa, M.; Hua, W.; Juwen, H.; Min, X.; Chunjie, H. *J. Hazard. Mater.* **2006**, *B136*, 502.
4. Sum, E. Y. L. *JOM* **1991**, *43*, 53.
5. Liang, P.; Yuana, L.; Yangb, X.; Zhouc, S.; Huang, X. *Water Res.* **2013**, *47*, 2523.
6. Nasefa, M. M.; Güven, O. *Prog. Polym. Sci.* **2012**, *37*, 1597.
7. Harris, N. D. U.S. Pat. 3,872,067 **1975**.
8. Parajuli, D.; Kunathai, K.; Adhikari, C. R.; Inoue, K.; Ohto, K.; Kawakita, H.; Funaoka, M.; Hirota, K. *Miner. Eng.* **2009**, *22*, 1173.
9. Syed, S. *Hydrometallurgy* **2012**, *115*, 30.
10. Dorfner, K. *Ion Exchangers*; Walter de Gruyter: Berlin, **1991**.
11. Pepper, K. W.; Paisley, H. M.; Young, M. A. *J. Appl. Chem.* **1956**, *844*, 4097.
12. Concha-Barrientos, M.; Nelson, D. I.; Driscoll, T.; Steenland, N. K.; Punnett, L.; Fingerhut, M. A.; Prüss-Üstün, A.; Leigh, J.; Tak, S.; Corvalan, C. *Selected Occupational Risk Factors in Comparative Quantification of Health Risk*; World Health Organisation: Geneva, **2004**.
13. Drew, R. T.; Laskin, S.; Cappiello, V. *Arch. Environ. Health* **1975**, *30*, 61.
14. Subramonian, S. *React. Funct. Polym.* **1996**, *29*, 129.
15. Cyganowski, P.; Jermakowicz-Bartkowiak, D. *Sep. Sci. Technol.* **2014**, *49*, 1689.
16. Jermakowicz-Bartkowiak, D. *React. Funct. Polym.* **2005**, *65*, 135.
17. Jermakowicz-Bartkowiak, D.; Kolarz, B. N. *Polimery* **2013**, *7–8*, 524.
18. Jermakowicz-Bartkowiak, D.; Kolarz, B. N. *Eur. Polym. J.* **2002**, *38*, 2239.

19. Dominguez, L.; Economy, J.; Benak, K.; Mangun, C. L. *Polym. Adv. Technol.* **2003**, *14*, 632.
20. Balakrishnan, T.; Ford, W. T. *J. Appl. Polym. Sci.* **1982**, *27*, 133.
21. Balakrishnan, T.; Murugan, E. *J. Appl. Polym. Sci.* **2002**, *41*, 347.
22. Revillon, A.; Guyot, A.; Prato, P.; Yuan, Q. *React. Polym.* **1989**, *10*, 11.
23. Cyganowski, P.; Jermakowicz-Bartkowiak, D.; Chęćmanowski, J.; Kujawska, M.; Bryjak, M. *Chin. J. Chem.* **2015**, *33*, 594.
24. Cyganowski, P.; Jermakowicz-Bartkowiak, D.; Bryjak, M. Polish Patent Office, Patent Application Under Number P.410196 (2014).
25. Cyganowski, P.; Jermakowicz-Bartkowiak, D.; Chęćmanowski, J. *Acta Chim. Slov.* **2015**, *62*, 672.
26. Wojaczynska, M.; Kolarz, B. N. *J. Appl. Polym. Sci.* **1995**, *56*, 433.
27. Jermakowicz-Bartkowiak, D.; Cyganowski, P. *Solvent Extr. Ion Exch.* **2015**, *33*, 510.
28. Campos, K.; Vincent, T.; Bunio, P.; Trochimczuk, A.; Guibal, E. *Solvent Extr. Ion Exch.* **2008**, *26*, 570.
29. Ho, Y. S. *Scientometrics* **2004**, *59*, 171.
30. Schiewer, S.; Patil, S. B. *Bioresour. Technol.* **2008**, *99*, 1896.
31. Ho, Y. S. *J. Hazard. Mater.* **2006**, *136*, 681.
32. Shi, K.; Wang, X.; Guo, Z.; Wang, S.; Wu, W. *Colloids Surf. A* **2009**, *349*, 90.
33. Schulze, R. G. *JOM* **1984**, *36*, 62.
34. Sánchez, J. M.; Hidalgo, M.; Salvadó, V. *Solvent Extr. Ion Exch.* **2000**, *18*, 1199.
35. Wolska, J.; Bryjak, M. *Desalination* **2011**, *283*, 193.
36. Kjeldahl, J. Z. *Anal. Chem.* **1883**, *22*, 366.
37. Jermakowicz-Bartkowiak, D.; Kolarz, B. N. *React. Funct. Polym.* **2011**, *71*, 95.
38. Vogel, A. I. *Handbook of Quantitative Inorganic Analysis*; Longman: London, **1978**.
39. Hecker, H. *J. Chromatogr* **1974**, *102*, 135.
40. Jing, X. S.; Liu, F. Q.; Yang, X.; Ling, P. P.; Li, L. J.; Long, C.; Li, A. M. *J. Hazard. Mater.* **2009**, *167*, 589.
41. Hubicki, Z.; Leszczyńska, M.; Łodyga, B.; Łodyga, A. *Miner. Eng.* **2006**, *19*, 1341.
42. Minczewski, J.; Marczenko, Z. *Analytical Chemistry. Trace Analysis*; Wydawnictwo Naukowe PWN: Warsaw, **2012**.
43. Helfferich, F. *Ion Exchange*; General Publishing Company: Toronto, **1995**.
44. Jermakowicz-Bartkowiak, D.; Cyganowski, P.; Leśniewicz, A.; Tylus, W.; Chęćmanowski, J.; Marcinowska, A. *J. Appl. Polym. Sci.* **2015**, *132*, 10190.
45. Jones, R. G.; Kahovec, J.; Stepto, R.; Wilks, E. S.; Hess, M.; Kitayama, T. *Compendium of Polymer Terminology and Nomenclature. IUPAC Recommendations 2008*; RCS Publishing: Cambridge, **2008**.