



# Direct modification of hydrogen/deuterium-terminated diamond particles with polymers to form reversed and strong cation exchange solid phase extraction sorbents

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## ABSTRACT

We describe direct polymer attachment to hydrogen and deuterium-terminated diamond (HTD and DTD) surfaces using a radical initiator (di-*tert*-amyl peroxide, DTAP), a reactive monomer (styrene) and a crosslinking agent (divinylbenzene, DVB) to create polystyrene encapsulated diamond. Chemisorbed polystyrene is sulfonated with sulfuric acid in acetic acid. Surface changes were followed by X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS) and diffuse reflectance Fourier transform infrared spectroscopy (DRIFT). Finally, both polystyrene-modified DTD and sulfonated styrene-modified DTD were used in solid phase extraction (SPE). Percent recovery and column capacity were investigated for both phenyl (polystyrene) and sulfonic acid treated polystyrene SPE columns. These diamond-based SPE supports are stable under basic conditions, which is not the case for silica-based SPE supports.

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## 1. Introduction

Solid phase extraction (SPE) is a widely used sample preparation and clean-up method in analytical chemistry, and numerous materials are potential candidates for SPE stationary phase/supports, including silica, highly cross linked polystyrene-divinylbenzene (PS-DVB) copolymer, carbon, and other oxide materials such as alumina, magnesia, and zirconia [1–9]. However, to one degree or another, all are somewhat lacking regarding their mechanical and/or chemical properties. For example, polymeric materials, especially if not highly cross-linked, swell in organic solvents. Silica and its silane adsorbates have low hydrolytic stability, especially at high and low pH, respectively. In contrast, diamond is an extraordinary material because of its mechanical stability at high pressure, excellent chemical stability over a very wide pH range, thermal stability, and general chemical stability and inertness [10–12]. These properties make it an attractive material for many applications, including, perhaps, as a stationary phase/support for SPE [13], HPLC [14–19], and capillary ultrahigh pressure liquid chromatography (UHPLC) [20,21]. There are a few recent examples of diamond's use in separation science [22]. Linford and coworkers modified diamond with polyallylamine for solid phase extraction [13]. This

primary amine modified diamond could then be further functionalized with hydrophobic isocyanates, and the resulting C<sub>18</sub> SPE adsorbate would extract pesticides from water [23]. A different hydrophobic SPE adsorbate could also be prepared by reacting di-*tert*-amyl peroxide (DTAP) with hydrogen- and deuterium-terminated diamond [24].

Telepchak [16] used natural diamonds as a stationary phase for reversed phase HPLC. Patel et al. [17] investigated a column (4.6 mm × 100 mm) packed with 3.8 μm diamonds for normal and reversed-phase HPLC. These two latter studies were successful in spite of their very low column efficiencies. Nesterenko et al. [14,18] also studied sintered diamonds as a stationary phase for HPLC and obtained more efficient separations compared to the previous studies by Telepchak [16] and Patel et al. [17]. In addition, Nesterenko studied the oxidative treatment of diamond particles for a cation-exchange column [15]. Liu [20] attempted to use polybutadiene-modified, and alkylated diamond in capillary UHPLC.

The attachment of various small molecules to diamond has now been reported [25–33]. However, there has been much less work on polymer modification of diamond surfaces. Gu electropolymerized diamond surfaces with an ultrathin film of a PANI-PAA (polyaniline/polyacrylate) copolymer [34]. In a multistep procedure, Steenackers et al. developed functional polymer grafts on oxidized ultrananocrystalline diamond (UNCD) surfaces using UV irradiation [35]. Cheng reported tethered polymer brushes on

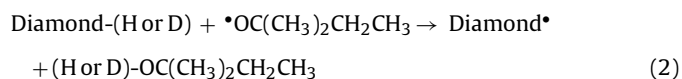
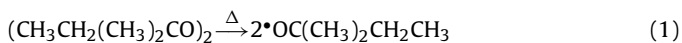
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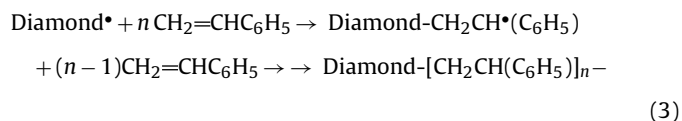
nanodiamond prepared from the reaction between surface carboxyl groups and the oxirane rings in triblock copolymers of *t*-butyl methacrylate, glycidyl methacrylate (GMA), and styrene [36]. Linford and coworkers, showed the adsorption and subsequent crosslinking or curing of poly(allylamine) on oxidized diamond [13]. Oxidized diamond powder can also be noncovalently coated with polylysine [37]. In a study directly related to the present work, some of us also demonstrated single-step polymer attachment onto hydrogen-terminated silicon using a radical initiator, an unsaturated monomer, and a crosslinking agent [38], where the resulting polymer films were 2–15 nm thick.

Here, we show a one-step polymerization on hydrogen-terminated diamond (HTD) [39,40] or deuterium-terminated diamond (DTD) using only unsaturated monomers and a peroxide initiator (di-*tert*-amyl peroxide, DTAP). The presence of a crosslinking agent, such as divinylbenzene (DVB), appears to enhance polymer growth. This work follows a careful study of the reaction of DTAP alone with HTD and DTD [24]. There is also a report of nanodiamond incorporation into bulk polymers via radical polymerization [41].

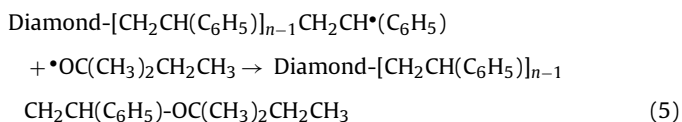
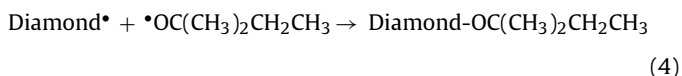
The mechanism by which polymer growth occurs on HTD or DTD is believed to be as follows. Radicals are created by the thermal decomposition of DTAP at its relatively weak O–O bond. Because the O–H bond is stronger than the C–H bond [42], these oxygen-centered radicals are believed to abstract hydrogen or deuterium from diamond surfaces, yielding carbon-centered radicals [24]:



The resulting surface radicals may then act as initiation sites for polymerization from the diamond surface.



Condensation of surface radicals with peroxy radicals could also take place to terminate reactive surface sites, as has previously been proposed on diamond surfaces [24]:



Other well-known termination events in radical polymerizations, such as combination and disproportionation are also expected. The presence of a bifunctional monomer, a crosslinker such as DVB, should also create additional surface sites for polymer grafting from solution and ultimately lead to tethered polymer films. DTAP fragments might also be expected to react with adsorbed polystyrene.

In essence, we are demonstrating that the conditions of a typical radical polymerization of unsaturated monomers will produce polymer grafting at HTD or DTD surfaces in a single chemical step, provided radical species derived from the initiator are capable of abstracting surface H or D atoms. After surface derivatization, polystyrene-functionalized diamond may be sulfonated with sulfuric acid. After demonstrating polymer growth on diamond surfaces,

both polystyrene-modified diamond and sulfonated, polystyrene-modified diamond are used in solid phase extraction, which is an important technique for sample preparation, purification, concentration, and cleanup, often preceding HPLC [1,2,43]. The resulting polymer-on-diamond stationary phase is expected to have excellent stability to both acids and bases.

## 2. Experimental

### 2.1. Reagents

With the exception that all monomers were passed through columns of inhibitor-removing material prior to use, all chemicals were used as received as follows: toluene (spectra grade, Aldrich, St. Louis, MO); methanol (spectra grade, Aldrich); H<sub>2</sub>SO<sub>4</sub> (95–98%, EMD, Gibbstown, NJ); HNO<sub>3</sub> (68–70%, EMD); glacial acetic acid (99%, Mallinckrodt Chemicals, Phillipsburg, NJ); di-*tert*-amyl peroxide (DTAP) (97%, Aldrich); styrene (99%, inhibited with 50 ppm *p*-*tert*-butylcatechol, Aldrich); divinylbenzene (DVB, 80%, remainder mostly 3- and 4-ethyl vinyl benzene, inhibited with 1000 ppm *p*-*tert*-butylcatechol, Aldrich); polystyrene (ave. *M<sub>n</sub>* ~ 192,000, Aldrich); 1-naphthylamine (99%, Aldrich); NaCl (reagent grade, Fisher, Fair Lawn, NJ); phosphate buffer: H<sub>3</sub>PO<sub>4</sub> (85%, EMD) and NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O (reagent grade, EMD).

The inhibitor-removing sorbent for removing *tert*-butylcatechol was obtained from Aldrich. Gas mixtures, including 6% hydrogen in argon (99.999%) and 5% deuterium in argon (99.999%), were purchased from Airgas (Radnor, PA).

### 2.2. Surface modification and characterization

#### 2.2.1. Preparation of deuterium-/hydrogen-terminated diamond powder

1.7 μm and 70 μm irregular diamond powders were provided by U.S. Synthetic, Orem, UT. Diamond powder was washed with a mixture of acids (90% H<sub>2</sub>SO<sub>4</sub> + 10% HNO<sub>3</sub>) at 80 °C for 4 h and then rinsed with distilled water [39]. After drying, the clean diamond powder was treated in flowing 5% D<sub>2</sub> (or 6% H<sub>2</sub>) in Ar at 900 °C in a tube furnace (the Mini-Mite, model number TF55030A-1, Thermo Electron, Waltham, MA) for 28 h. 6% hydrogen or 5% deuterium in argon is not a flammable mixture, and therefore safer to work with than pure H<sub>2</sub> or D<sub>2</sub> gas, which can form explosive mixtures with air. During the hydrogenation/deuteration, the diamond powder was shaken twice to expose all surfaces of the powders, and it was then cooled in flowing 5% D<sub>2</sub> (or 6% H<sub>2</sub>) in Ar. The resulting hydrogen/deuterium-terminated diamond powder was used as a starting material.

#### 2.2.2. Treatment of DTD with DTAP, styrene, and divinylbenzene (DVB)

A 50 mL solution of DTAP (0.05 M), styrene (0.75 M), and a crosslinking agent, DVB (0.025 M), in toluene was bubbled with nitrogen for 30 min prior to addition of hydrogen/deuterium-terminated diamond powder (0.5 g). Toluene is a good solvent for radical polymerizations because of its small chain transfer constant [44]. The temperature of the solution was raised to 110 °C. The solution was maintained at 110 °C for 24 h while being stirred under a reflux condenser. It was continuously purged with a gentle stream of nitrogen over the surface of the solution. The diamond powder was then removed from solution and washed thoroughly with toluene. Finally, the diamond powder was dried *in vacuo* at 80 °C overnight.

#### 2.2.3. Preparation of a thin polystyrene film on silicon surfaces

Polystyrene was dissolved in toluene (0.5% w/w) and spin coated onto silicon shards.

### 2.2.4. Sulfonation of polystyrene-functionalized diamond powder

The method of PS–DVB resin sulfonation described by Dumont and Fritz was followed [45,46]. Polystyrene-functionalized diamond powder (2 g) was slurried in 5 mL acetic acid followed by addition of 20 mL of concentrated sulfuric acid, which had been cooled in an ice bath. The reaction temperature was then set at 90 °C for 5 h, after which the slurry was poured over ice to quench the reaction. The diamond powder was filtered and washed with water until the pH of the water was neutral.

### 2.2.5. Characterization of the diamond surfaces

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was performed with an ION-TOF ToF-SIMS IV instrument using monoisotopic 25 keV  $^{69}\text{Ga}^+$  ions. X-ray photoelectron spectroscopy (XPS) was performed with a Surface Science SSX-100 X-ray photoelectron spectrometer with a monochromatic Al  $K_{\alpha}$  source and a hemispherical analyzer. An electron flood gun was employed for charge compensation. Survey scans as well as narrow scans were recorded with an 800  $\mu\text{m} \times 800 \mu\text{m}$  spot. For ToF-SIMS and XPS analyses the diamond powders were mounted onto double-sticky tape adhered to silicon wafers. FTIR spectra were obtained of coated 1.7  $\mu\text{m}$  diamond particles with a Magna-IR 560 spectrometer from Nicolet (Madison, WI). The resulting diffuse reflectance (DRIFT) spectra were collected from 400 to 4000  $\text{cm}^{-1}$ . For each spectrum, 64 scans were collected at a resolution of 4  $\text{cm}^{-1}$ . Spectra are presented with Kubelka-Munk units. Elemental analysis of sulfur and carbon was determined by a high temperature combustion analysis (Columbia Analytical Services, Tucson, AZ). Surface area measurements were performed by taking Brunauer–Emmett–Teller (BET) isotherm measurements using a Micromeritics instrument. Specific surface areas of the samples were determined from  $\text{N}_2$  adsorption at 77 K (Micromeritics TriStar II). The samples were degassed at 200 °C for 12 h prior to data collection.

## 2.3. Solid phase extraction (SPE)

### 2.3.1. Elution procedure

SPE of 1-naphthylamine was performed with a cartridge prepared in our laboratory. The packing material from a commercially available cartridge (Phenomenex Strata, 3 mL SPE standard tube) was replaced by our phenyl and sulfonated phenyl stationary phases. Accordingly, SPE cartridges (9.5 mm in diameter, 62 mm overall height, and 18 mm of packing material) were packed with ca. 2.5 g of the functionalized diamond particles, which were suspended in water or methanol and poured into the column. To improve the packing, the cartridges were washed with water or methanol under reduced pressure from the house vacuum during loading until the height of the packing material remained constant. Finally, the columns were dried using the house vacuum. Based on the packing volume and the amount of diamond used, the porosity of the packing bed was ca. 44%, which indicates the packing was highly efficient for our irregularly shaped particles. A control experiment showed that neither the plastic cartridges nor the frits retained the analyte (1-naphthylamine). The same volume of packing material was used in all of the experiments.

Prior to applying analyte, packed, polystyrene-coated diamond particles were conditioned with 6 column volumes of MeOH, followed by 6 column volumes of water. 50  $\mu\text{L}$  of 1-naphthylamine (1 mg/mL) in ca. 99:1 water:methanol was then loaded onto the column. The column was washed with water and finally eluted by gravity elution (<1 min) with methanol. This phenyl column could be reused multiple times in this fashion after washing with MeOH.

For the sulfonated polystyrene-diamond stationary phase, the columns were first conditioned with 6 column volumes of methanol, and then with six column volumes of phosphate buffer (10 mM, pH = 1.9). 50  $\mu\text{L}$  of 1-naphthylamine (1 mg/mL) in phos-

phate buffer (10 mM, pH = 1.9) was then applied to the column. After washing with phosphate buffer (10 mM, pH = 1.9), the analyte was eluted by gravity elution (<1 min) with NaCl-containing phosphate buffer (10 mM, pH = 1.9, NaCl, ionic strength 0.2 M):methanol (v/v, 1:1).

In practice, sulfonated, polystyrene-modified diamond SPE sorbents could be repeatedly used without noticeable degradation. Before each reuse, a column was washed with NaCl-containing phosphate buffer (10 mM, pH = 1.9, NaCl, ionic strength 0.2 M):methanol (v/v, 1:1) several times to regenerate it.

### 2.3.2. Breakthrough curves and column capacity

The columns, including the polystyrene-functionalized and sulfonated polystyrene-functionalized SPE columns, were first conditioned using the procedures mentioned above. After conditioning, the solution of 1-naphthylamine (0.01 mg/mL) in ca. 99:1 water:methanol was passed through the polystyrene-functionalized SPE column, and the solution of 1-naphthylamine dissolved in phosphate buffer (pH = 1.9) (0.02 mg/mL) was passed through the sulfonated polystyrene column, both at a constant flow rate. Equal volumes (fractions) eluting from the column were collected in separate vials. Finally, these fractions were analyzed by ESI–MS.

The breakthrough curves herein, which generally have sigmoidal shapes, are plots of solution volumes eluted from an SPE cartridge vs. the  $[\text{M}+1]^+$  mass spectral peak area of the analyte in each fraction. The breakthrough volume was calculated from the point on the curve corresponding to 5% of the average value at the maximum (the plateau region). The column capacity was calculated by multiplying the breakthrough volume by the corresponding concentration of analyte.

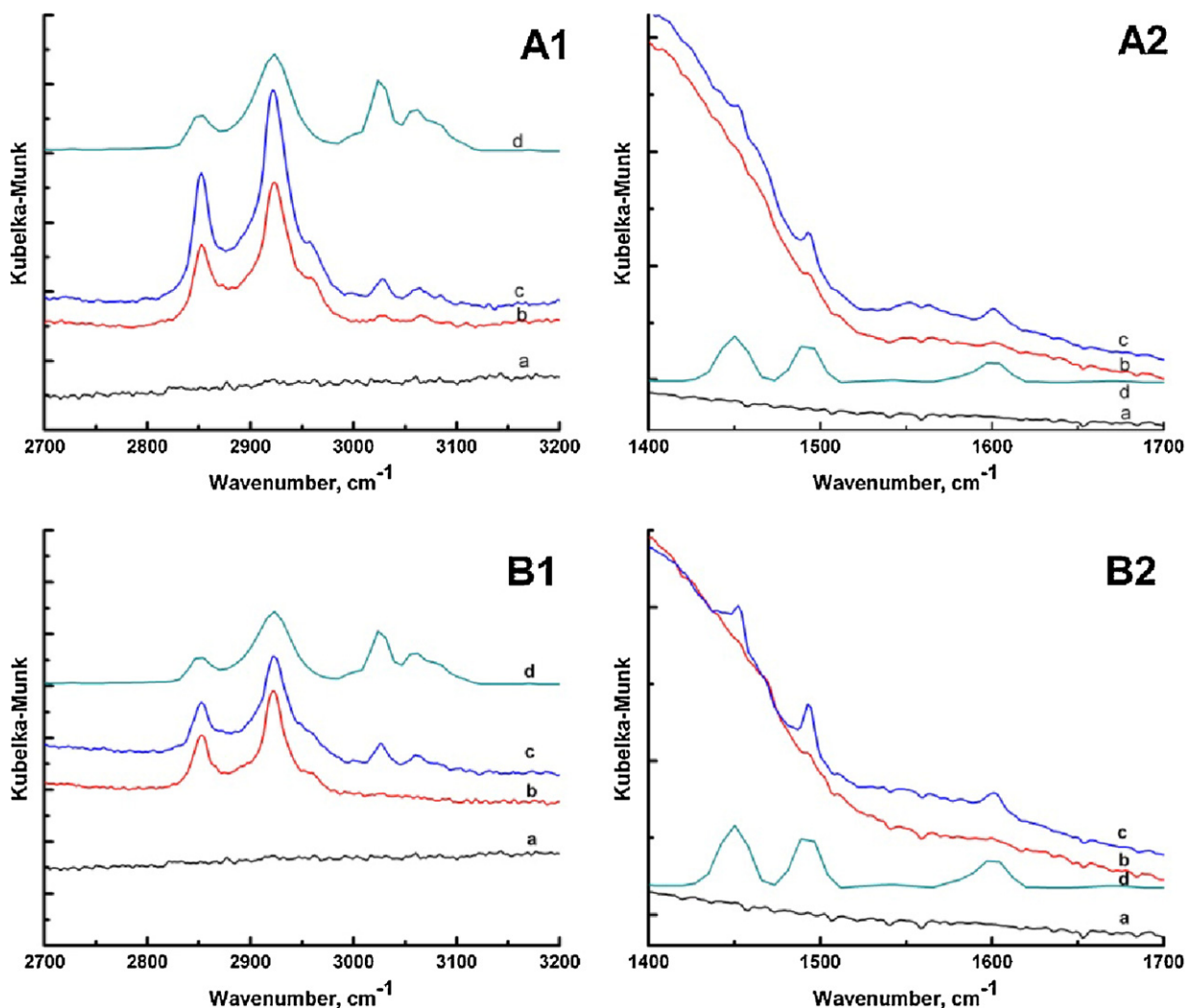
### 2.3.3. Percent recovery

For phenyl (polystyrene-coated) SPE columns, 50  $\mu\text{L}$  of 1-naphthylamine (1 mg/mL) in ca. 99:1 water:methanol was added to the column with a micropipette. The column was then extracted with methanol. A reference solution was created by adding 50  $\mu\text{L}$  of 1-naphthylamine (1 mg/mL) in water (~1% methanol) directly to the extracted sample from a blank matrix. These two solutions were then analyzed by ESI–MS and the  $[\text{M}+\text{H}]^+$  peak for each respective analyte was integrated. The division of these two peak areas multiplied by 100 gave the % SPE recovery.

For the sulfonated polystyrene SPE column, 50  $\mu\text{L}$  of 1-naphthylamine (1 mg/mL) in phosphate buffer (10 mM, pH = 1.9) was added to the column (under these conditions the analyte will be protonated). The column was then extracted with NaCl-containing phosphate buffer (10 mM, pH = 1.9, NaCl, ionic strength 0.2 M):methanol (v/v, 1:1). A reference solution was created by adding the same amount of analyte directly to the extracted sample from a blank matrix. The remainder of the analysis and calculations were the same as above.

### 2.3.4. Electrospray MS (ESI–MS)

Electrospray MS (ESI–MS) was performed using an Agilent Technologies LC/MSD TOF system by direct infusion of several microliters of sample along with the mobile phase: 75% MeOH and 25% water, with 5 mM ammonium formate. A steel ES ionization needle was used in positive-ion mode, and the charging voltage and the capillary voltages were set at 900 V and 3500 V, respectively. The nebulizer was set at 35 psi, the gas temperature was 350 °C, and the skimmer was operated at 60 V. The flow rate of the nitrogen drying gas was 12 L/min. One survey scan was collected per second over a mass range of  $m/z$  100–1200.



**Fig. 1.** A1 and A2: (a) DRIFT spectrum of deuterium-terminated diamond powder, (b) DRIFT spectrum of a control experiment of deuterium-terminated diamond powder exposed to styrene without di-*tert*-amyl peroxide for 1 day at 110 °C, (c) DRIFT spectrum of deuterium-terminated diamond powder reacted with styrene and di-*tert*-amyl peroxide for 1 day at 110 °C, and (d) IR spectrum of polystyrene. B1 and B2: (a) DRIFT spectrum of deuterium-terminated diamond powder, (b) DRIFT spectrum of a control experiment of deuterium-terminated diamond powder exposed to styrene/DVB without di-*tert*-amyl peroxide for 1 day at 110 °C and (c) DRIFT spectrum of deuterium-terminated diamond powder reacted with styrene/DVB and di-*tert*-amyl peroxide for 1 day at 110 °C, and (d) IR spectrum of polystyrene.

#### 2.4. Stability test

Polystyrene- and sulfonated polystyrene-coated diamond particles, and commercial polymer-based and silica-based SPE sorbents were immersed in both 1 M NaOH and 1 M HCl solution for 70 h to evaluate their stability under strongly basic or acidic conditions. Methanol (10% by volume) was added to the solutions used to test the polystyrene-coated diamond so that the solutions would better wet the particles. These stationary phases were characterized by XPS and DRIFT.

### 3. Results and discussion

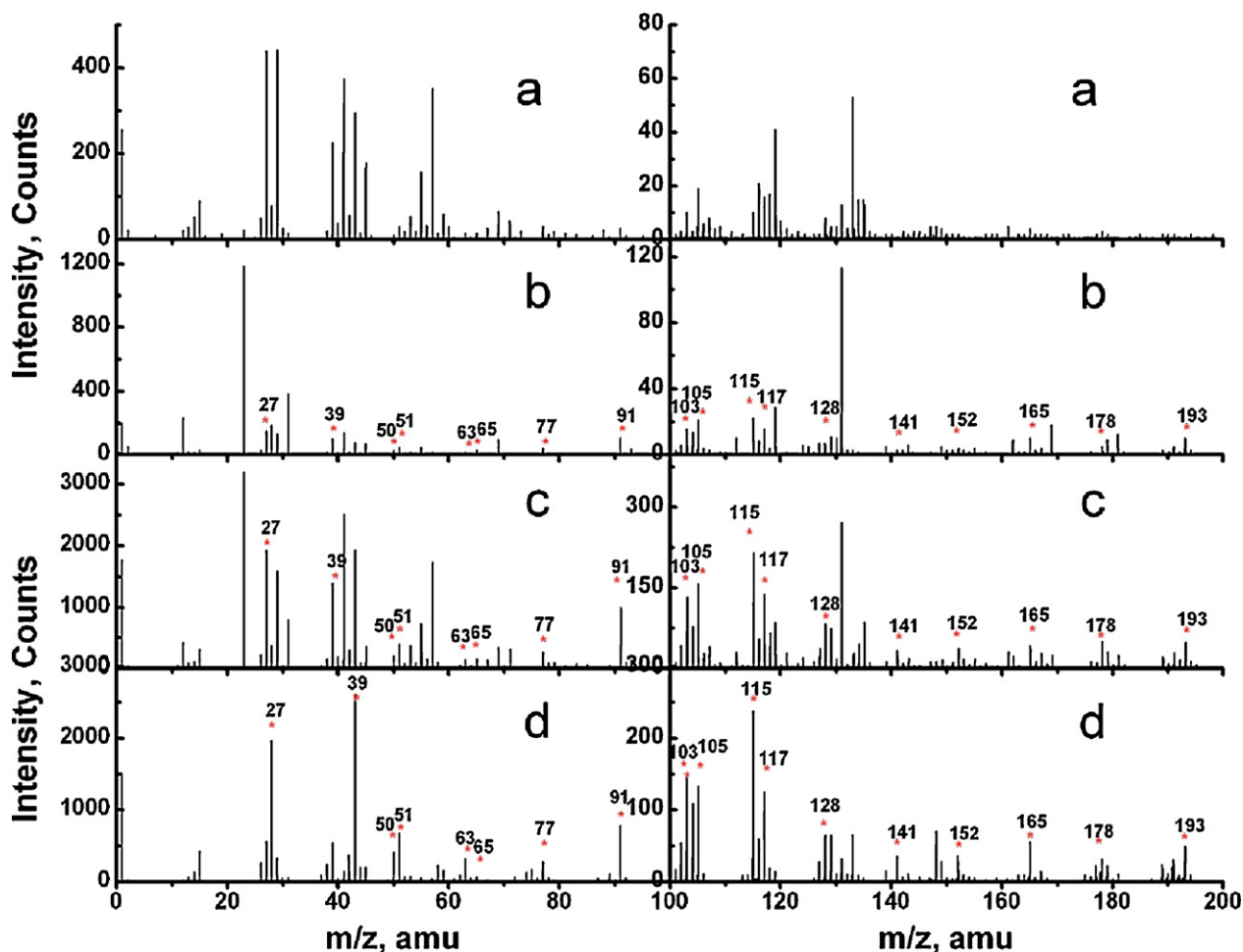
#### 3.1. Reaction of deuterium-terminated diamond (DTD) with DTAP and unsaturated monomers with and without a crosslinker (DVB)

Panels A1 and A2 of Fig. 1 show the diffuse reflectance Fourier transform infrared (DRIFT) spectra of DTD reacted with styrene in the presence and absence of di-*tert*-amyl peroxide (DTAP). DTD is an excellent substrate for these studies because of its clean baseline in the C–H IR stretching region. Panels B1 and B2 of Fig. 1 similarly show the infrared spectra from these reactions that also con-

tained DVB. In both cases, C–H stretches assigned to aromatic rings (3000–3200  $\text{cm}^{-1}$ ) and alkyl chains (2800–3000  $\text{cm}^{-1}$ ) appear after the reactions, where such stretches were not observable in the spectra of unmodified DTD (Figs. 1A1-a and B1-a) – the IR spectrum of a polystyrene standard is also given in Fig. 1 as a comparison for the functionalized diamond powders. These spectra also suggest that the presence of DVB somewhat increases the amount of polystyrene that deposits on the diamond surface.

For the control reactions without peroxide initiator (DTAP) of DTD with styrene or with styrene and DVB, DRIFT showed either much smaller or no aromatic =C–H stretches (3000–3200  $\text{cm}^{-1}$ ) and little or no sign of the other characteristic peaks (aromatic ring-stretching vibrations) from polystyrene at  $\sim 1450 \text{ cm}^{-1}$ ,  $\sim 1500 \text{ cm}^{-1}$  and  $\sim 1600 \text{ cm}^{-1}$ . These control reactions show that the surface reaction is limited or absent when the radical initiator is absent and/or that non-specific adsorption of any polymerized species is low.

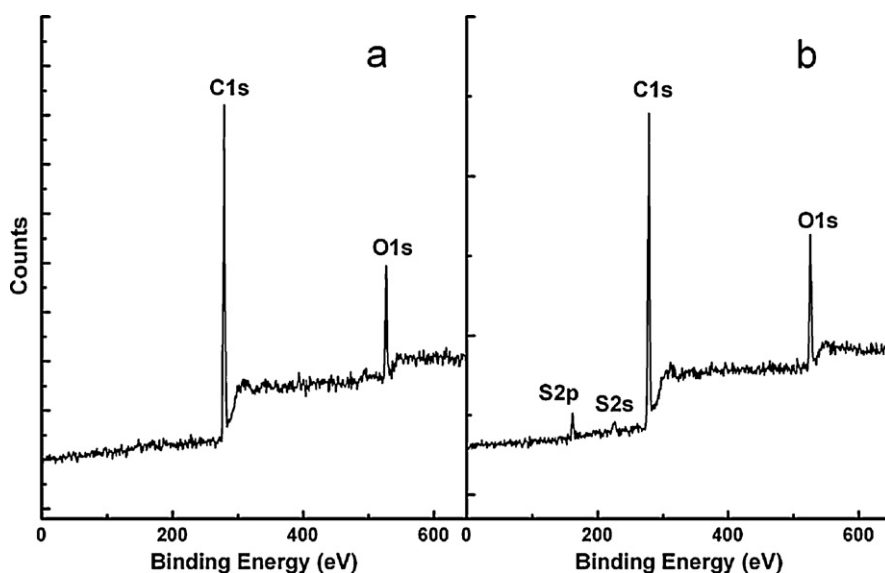
Fig. 2 shows positive ion ToF-SIMS spectra of DTD and DTD functionalized by styrene or by styrene/DVB under peroxide initiation. There are some hydrocarbon peaks in the ToF-SIMS spectra of DTD, where hydrocarbon contamination is common on most materials. However, after reaction with styrene and DTAP, a series of hydro-



**Fig. 2.** ToF-SIMS positive ion spectra from 0–100 amu and 100–200 amu of: (a) DTD, (b) DTD reacted with styrene and DTAP, (c) DTD reacted with styrene, DTAP and DVB, and (d) a thin film of polystyrene (made by spin-coating PS onto a shard of silicon).

carbon peaks that is characteristic of polystyrene (marked by a red star) appears (Figs. 2b and d) (For interpretation of the references to color in this sentence, the reader is referred to the web version of the article.). The positive ion ToF-SIMS spectrum of DTD after reaction with styrene/DVB shows these characteristic signals of polystyrene

in an even more dominant fashion (Figs. 2b and c). This is especially true for the highly characteristic, higher mass ions. In contrast, in the spectrum of the DTD, there is little but noise in the high mass region. These SIMS results are a reasonable chemical confirmation of the FTIR results shown in Fig. 1.



**Fig. 3.** XPS survey spectra of diamond powders: (a) polystyrene-functionalized diamond powder and (b) sulfonated PS-DVB-functionalized diamond powder.

**Table 1**  
Compositions (atom percentages of elements detected by XPS) of the surfaces of modified diamond powders.

	C%	O%	S%
Polystyrene (PS)	86.7	13.3	Not detected
Sulfonated PS	86.7	11.5	1.8
Sulfonated PS–DVB	81.5	15.6	2.9

While the negative ion ToF-SIMS spectra are somewhat less conclusive in showing a reaction between DTD and styrene or styrene/DVB (negative ion spectra are usually not as rich in the more chemically specific (molecular) fragments as positive ion spectra), they are still consistent with the proposed surface transformations. First, there is an obvious deuterium peak from the DTD. After the reaction with styrene or with styrene/DVB under peroxide initiation, the ratio of  $H^-/D^-$  is increased from 0.9 (before) to 2.4–6.6, presumably because deuterium atoms are abstracted by peroxy radicals allowing polystyrene growth on the diamond surfaces. Also, the ratio of  $C^-/O^-$  is 2.1 for polystyrene functionalized diamond and 3.0 for PS–DVB functionalized diamond, presumably because more carbon is introduced in the styrene–DVB reaction.

No thickness measurements, *per se*, of the polymer coatings were performed. However, our previous study of the reaction of styrene/DVB and a radical initiator with hydrogen-terminated silicon suggests that (i) the polymer thickness would be on the order of 5–10 nm, (ii) that the presence of DVB should lead to thicker polymer films, and (iii) that polymer growth should be conformal and smooth on the particles because of the extremely smooth films that were obtained previously on hydrogen-terminated silicon [38].

All of these diamond materials were also probed by XPS. The O1s/C1s ratios, as measured in XP narrow scans, decrease from 0.162 for diamond functionalized by polystyrene and DTAP to 0.088 for diamond functionalized with PS–DVB and DTAP, again suggesting that the presence of the crosslinker leads to increased polymer (carbon) deposition.

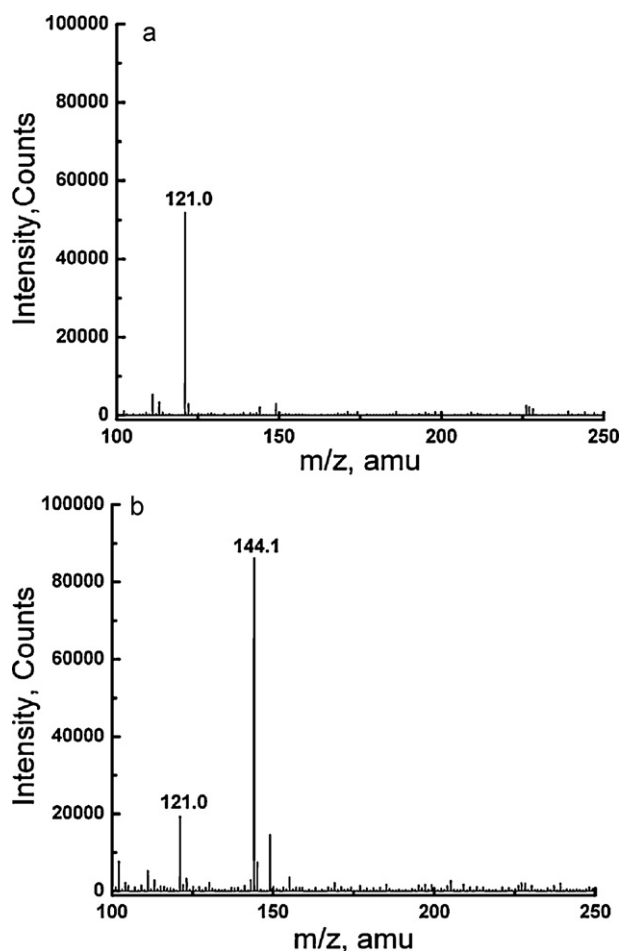
Hence, DRIFT, ToF-SIMS and XPS all suggest that abstraction of deuterium atoms from the diamond surface by the radical species derived from DTAP in the presence of a monomer, styrene, leads to polymerization on the diamond surface. DVB appears to act as a crosslinker, increasing the thickness of polystyrene on the diamond surfaces.

Hydrogen-terminated diamond particles were also functionalized using the same procedures that were applied to DTD, and the same results that were obtained in this section, as well as the following section were obtained.

### 3.2. Sulfonation of polystyrene-functionalized diamond powder

Polystyrene (PS) and PS–DVB functionalized diamond powder were sulfonated by immersion in acetic acid and concentrated sulfuric acid at 90 °C for 5 h [45,46]. Fig. 3b shows XPS of sulfonated styrene/DVB-functionalized diamond particles that contains obvious sulfur signals, where no sulfur was discernable by XPS in either the styrene- or styrene/DVB-functionalized diamond materials prior to sulfonation (Fig. 3a). The increased sulfur-to-carbon ratio in the sulfonated PS/DVB-modified diamond powder over the sulfonated PS-modified diamond powder (no DVB) also suggests that thicker films are formed when the crosslinker (DVB) is used (Table 1).

Note the unusual result of the oxygen content of the polystyrene-coated diamond particles *decreasing* after sulfonation. This result was reproducible and is attributed to the use of toluene as the rinse solvent after surface polymerization. That is, toluene is a fine choice of solvent for removing unbonded polystyrene and the like, but it will be less effective in removing highly polar, *e.g.*, oxygenated, species. It would appear that some such species remain



**Fig. 4.** Positive ion ESI-MS spectra of fractions taken from PS–DVB-modified diamond SPE stationary phases: (a) fraction eluted with water (no analyte present). (b) Fraction eluted with methanol, showing the analyte peak (1-naphthylamine) at 144 amu.

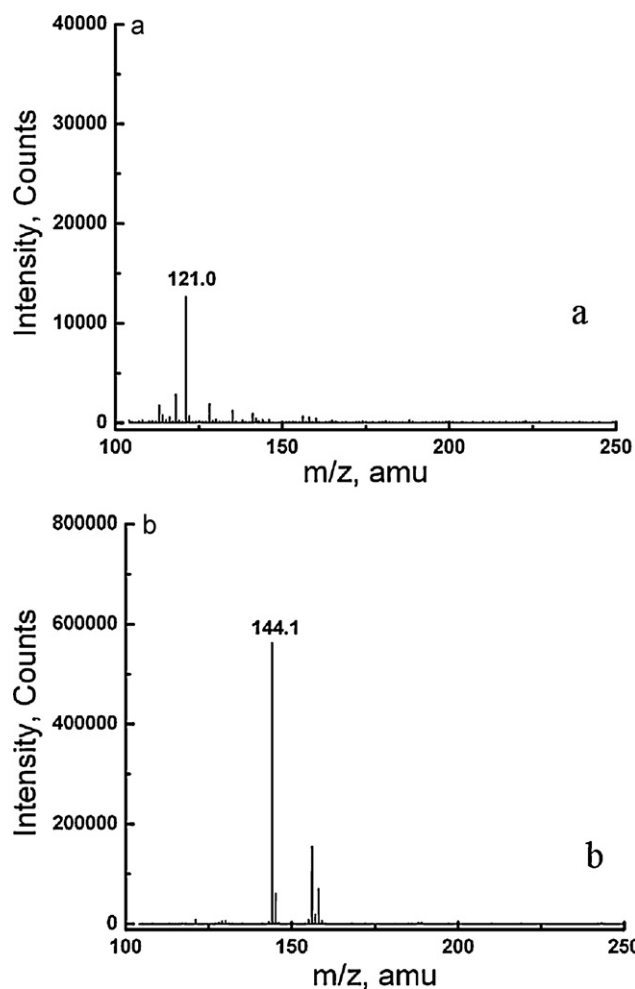
on the particles after polymerization and that these materials are subsequently removed in the highly polar solvent/reagent used for sulfonation (a mixture acetic acid and sulfuric acid).

### 3.3. Sulfur surface coverage

The surface coverage of sulfur in the PS/DVB particles was estimated in two ways: elemental analysis/BET and X-ray photoelectron spectroscopy. The elemental analysis showed the concentration of sulfur to be low (<0.005 wt.%), and the surface area of these particles by BET was 0.09 m<sup>2</sup>/g. These numbers allowed an estimation of the sulfur coverage of the particles to be obtained from the Berendsen and de Galan equation as 17 μmol/m<sup>2</sup>. XPS suggested a somewhat higher surface coverage of sulfur. That is, a rough estimate of 24 μmol/m<sup>2</sup> was derived from the atom% sulfur in the particles found by XPS (the 2.9% value in Table 1), the density of polystyrene (*ca.* 1 g/cm<sup>3</sup>), and an estimate of the escape depth of a photoelectron in polystyrene (*ca.* 10 nm). These numbers suggest a fairly high degree of sulfonation for the particles.

### 3.4. Solid phase extraction with PS–DVB-modified and sulfonated, PS–DVB-modified diamond

PS–DVB-coated diamond particles (a reversed-phase material) and sulfonated PS–DVB-coated diamond particles (a strong cation ion exchange (SCX) material) were loaded into columns and used for solid phase extraction. A demonstration of the reten-

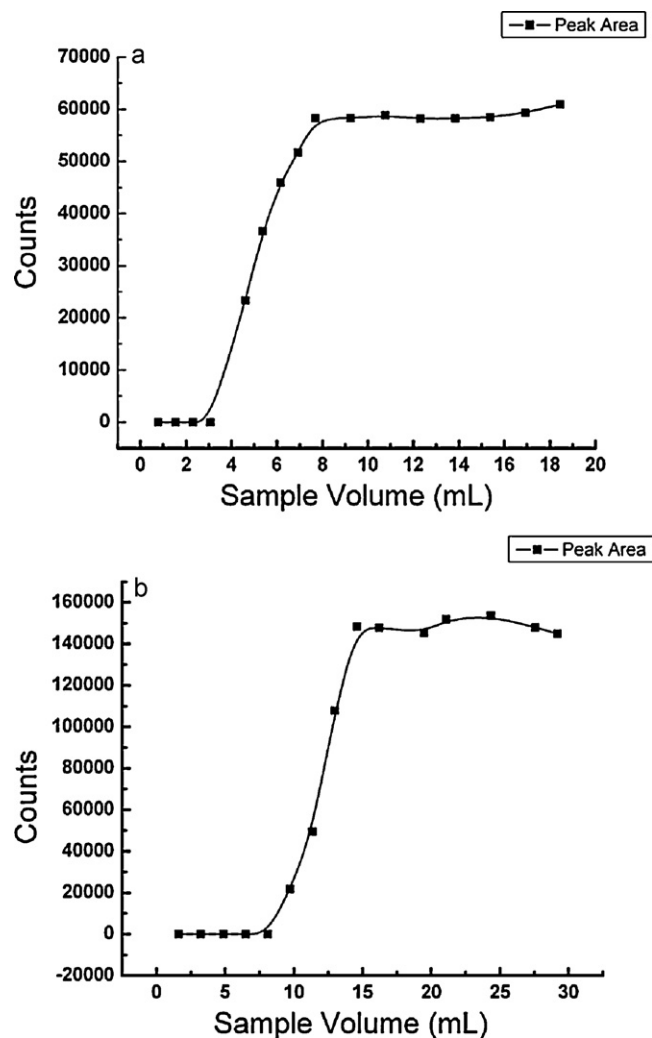


**Fig. 5.** Positive ion ESI-MS spectra of SPE fractions taken from a sulfonated PS-DVB diamond SPE phase: (a) fraction eluted with the phosphate buffer (10 mM, pH = 1.9) showing no analyte, (b) the analyte (1-naphthylamine) eluted with a higher ionic strength phosphate buffer, which also contained an organic solvent [(10 mM, pH = 1.9, NaCl, ionic strength 0.2 M):methanol (v/v, 1:1)].

tion and release of an analyte was performed with the analyte 1-naphthylamine. These PS-DVB and sulfonated diamond columns were reusable; the columns could be used multiple times without any sign of degradation.

After conditioning, PS-DVB-coated columns were loaded with 1-naphthylamine, the column was washed with water, and the analyte was eluted with methanol. Electrospray ionization mass spectrometry (ESI/MS) was used to confirm the presence or absence of the analytes in the fractions that were taken, *i.e.*, the  $[M+1]^+$  peak at 144 amu of 1-naphthylamine appeared in the methanol fraction, while it was not present in the pre-wash liquid (Fig. 4a and b). As controls, the same procedure was applied to two other SPE columns, which were packed with hydrogen or deuterium-terminated diamond powder [27]. For these two columns, the analyte (1-naphthylamine) eluted (immediately) in the first solvent (water). Thus, 1-naphthylamine is retained by a PS-DVB-functionalized diamond SPE sorbent, but not by hydrogen/deuterium-terminated diamond. While both materials should be hydrophobic, the PS-DVB-coated diamond should offer  $\pi$ - $\pi$  analyte-stationary phase interactions, and also increased analyte capacity, assuming the analyte can diffuse into the PS-DVB coating.

The sulfonated styrene column was first conditioned and 1-naphthylamine in phosphate buffer was loaded onto the column.



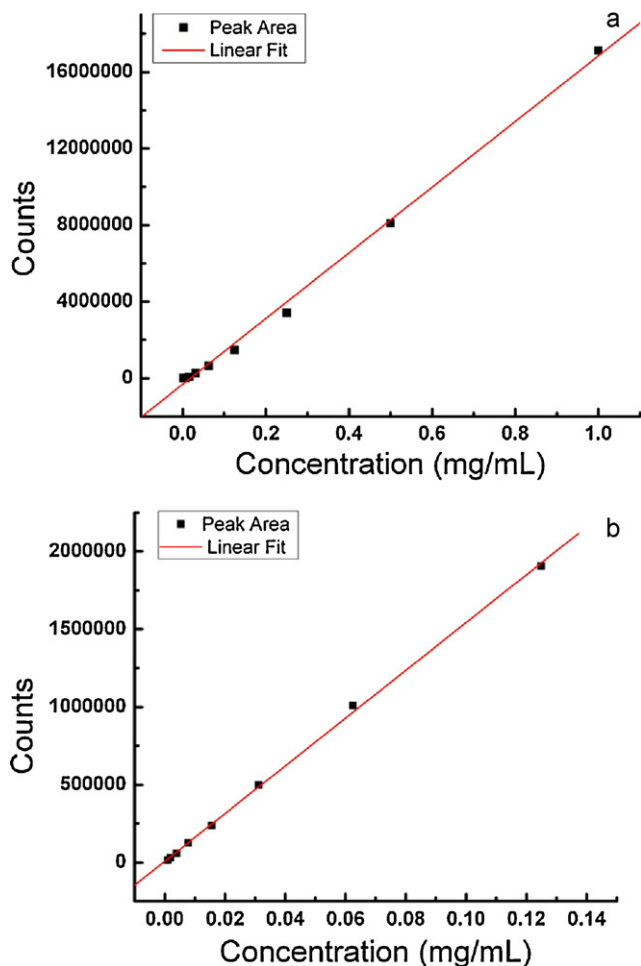
**Fig. 6.** Breakthrough curves for 1-naphthylamine on PS-DVB- (a) and sulfonated polystyrene- (b) coated 70  $\mu$ m diamond particles. Each point represents the peak area of the analyte from the corresponding positive ion ESI-MS spectrum.

Fig. 5 shows ESI/MS spectra of the water and phosphate buffer (10 mM, pH = 1.9, NaCl, ionic strength 0.2 M):methanol (v/v, 1:1) fractions eluted from sulfonated PS-DVB-coated diamond. The analyte peak at 144 amu is not present in the water fraction, but is dominant in the spectrum from the NaCl-containing phosphate buffer fraction. The peak at  $m/z$  121 in Figs. 4 and 5 is from a reference material added in the Agilent MS instrument. In contrast to these results, for SPE columns made of either PS-DVB-coated diamond powder or hydrogen/deuterium-terminated diamond powder, the analyte eluted directly in the first fraction (phosphate buffer, 10 mM, pH = 1.9). These results suggest the expected ionic interaction between the analyte and the sulfonic acid group.

Breakthrough curves (Fig. 6) were obtained for SPE columns, using 1-naphthylamine as an analyte, to determine breakthrough volumes of the phenyl and the strong cation exchange SPE columns. (It should be noted that low column capacities are to be expected for the nonporous particles employed in this study.) The breakthrough volume was taken from the point on the breakthrough curve at 5% of the average value at the breakthrough curve plateau region. (Fig. 7 shows the linear range of the instrument for two different solutions of 1-naphthylamine illustrating that the breakthrough curves are within these ranges.) From the breakthrough curves, column capacities for the phenyl and cation exchange SPE columns were determined to be 31.5 and 80  $\mu$ g, respectively.

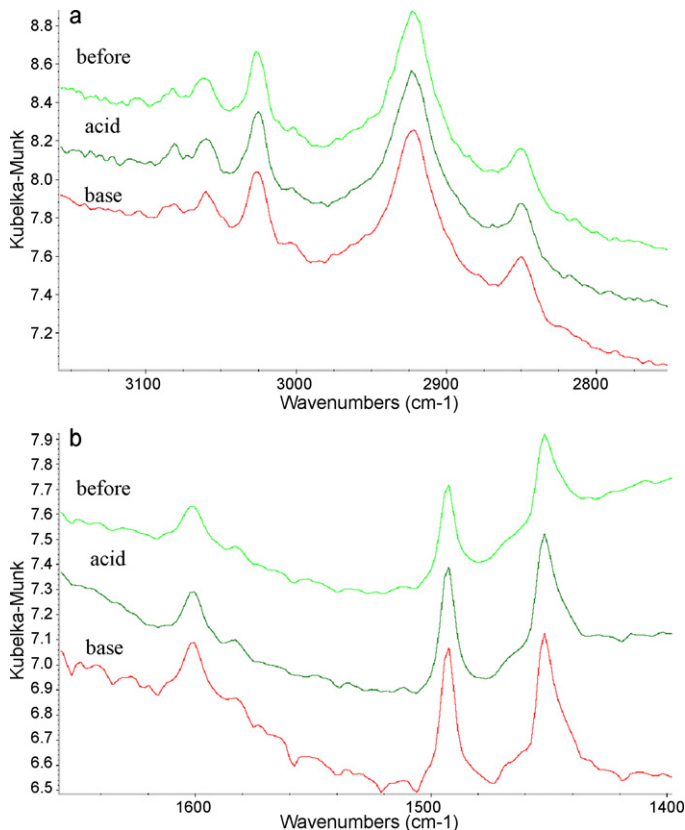
**Table 2**  
Stability test results: S2p/C1s ratio from XPS.

Type	Stationary phase	Original	In 1 M HCl (70 h)	In 1 M NaOH (70 h)
Diamond	Sulfonated PS	0.018 ± 0.000	0.019 ± 0.001	0.018 ± 0.002
	Sulfonated PS-DVB	0.036 ± 0.001	0.038 ± 0.001	0.038 ± 0.001
Commercial	Silica SCX	0.16 ± 0.03	0.15 ± 0.02	Dissolved
	Polymer SCX	0.017 ± 0.002	0.015 ± 0.00	0.016 ± 0.000



**Fig. 7.** Linear relationship between signal and concentration for 1-naphthylamine in water (a) and phosphate buffer (pH = 1.9) (b) from the positive ion ESI-MS spectra.

The percent recoveries of the phenyl and cation exchange SPE columns were 65.8% and 101% (our best retention measurements) – much of the analyte (1-naphthylamine) can be recovered from phenyl SPE columns, and all of it from the strong cation exchange material. More specifically, we also comment here on the elution of the analyte (1-naphthylamine) by phosphate buffer with NaCl (pH = 1.9) only, or with the mixture of the phosphate buffer with NaCl (pH = 1.9) and methanol (v/v, 1:1). The percent recoveries after eluting with these buffers are around 60–70% and 101%, respectively. Thus, complete recovery of the analyte is found when 50% percent methanol is added to the buffer. These results suggest that there are multiple interactions between the analyte and the stationary phase in the SCX SPE column, which include ionic interactions with the sulfonic acid groups and non-polar interactions with the aromatic ring. When multiple mechanisms are active, disruption of more than one retention mechanism improves analyte recovery.



**Fig. 8.** IR spectra of polystyrene-functionalized diamond before and after immersion in solutions of 1 M HCl (acid) or 1 M NaOH (base).

### 3.5. Stability of diamond stationary phases

One reason for the current interest in diamond materials as a solid support for SPE and HPLC is its inert nature. Of course, one would expect the stationary phase (coating) to match this high stability, at least under the conditions that might be encountered in SPE and HPLC. Accordingly, chemical stability tests were performed on polystyrene-coated and sulfonated polystyrene-coated diamond particles by immersing them into acidic or basic solutions for 70 h. These conditions were chosen because silica is unstable at high pH, and silane coatings on silica hydrolyze at low pH. Following these tests, IR spectra of polystyrene-coated diamond particles showed little or no change in the intensities of the C–H stretches and the ring vibrations (Fig. 8). These results indicate that little or no polystyrene is removed by strong base or acid, *i.e.*, that polystyrene-coated diamond particles are stable to strong acid and base. For sulfonated polystyrene, the S2p-to-C1s ratio by XPS remains essentially constant after these stability tests, whether it was prepared from polystyrene or PS-DVB (Table 2). These results were compared to the stability of a commercially-available SPE stationary phase (Phenomenex Strata SCX, 55 μm, 70 Å, silica based), which was stable in acid, but after immersion in 1.0M NaOH for 8 h completely dissolved. To further verify the dissolution of these particles, the resulting clear solution was filtered. It easily passed



through the filter, leaving no material behind. Polymer-based particles from Phenomenex were also immersed in 1 M HCl and 1 M NaOH for 70 h. Their S2p/C1s ratios remained essentially constant. Thus, sulfonated polystyrene on diamond has the same solid stability in acid and base as a commercially-available polymer-based SCX SPE material, while being (overall) much more stable than a silica-based SPE sorbent.

#### 4. Conclusions

The new method introduced in this paper appears effective in growing polymers on deuterium-/hydrogen-terminated diamond powder using a simple, one-step procedure. The surface radicals that should be produced at the diamond surface appear to react with monomers, crosslinkers, and perhaps growing polymer chains in solution to tether them to the surface of the diamond powder. The incorporation of some crosslinking in these adsorbed polymer films through DVB appears to increase film thickness. Some non-specific adsorption of the polymer also seems to occur. The one-step method for growing polymers on deuterium-/hydrogen-terminated diamond powders shown here should provide a simple, inexpensive way to covalently modify diamond powder with tailored polymers produced from a variety of known monomers. Diamond powder modified with phenyl and sulfonated phenyl moieties can be used as a reversed-phase or as a strong cation ion exchange stationary phase, respectively. The performance, column capacity, and percent recovery of these two SPE columns were studied using 1-naphthylamine. These diamond stationary phases have excellent stability in both highly acidic and highly basic media.

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