Preparation and characterization of highly polar polymeric sorbents from styrene-divinylbenzene and vinylpyridine-divinylbenzene for solid-phase extraction of polar organic pollutants

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Summary

This paper explores the synthesis of styrene-divinylbenzene resins with different surface areas and the influence of these surface areas on their performance in the solid-phase extraction of polar compounds from water samples. As expected, increasing the surface areas increases the retention capability of polar compounds.

To improve retention properties, we used 4-vinylpyridine instead of styrene in the polymerization and evaluated the influence of the sorbent polarity and surface area on the retention properties. We have found that a compromise is required between the percentage of 4-vinylpyridine, which increases the polarity of the sorbent, and the percentage of divinylbenzene, which increases the surface area. In solid-phase extraction of polar compounds, the results are best for the polymer containing 2.14 % of N and having a surface area of 710 m^2/g.

Introduction

Since they first came available in the late 1950s, macroporous polymers have been used in numerous applications as polymeric reagents and catalysts, supports for solid-phase synthesis, ion-exchangers and chromatographic packings.[1] They are characterized by a permanent porous structure which persists in the dry state unlike other polymers, which require solvent swelling to become porous. These polymers are typically obtained by free radical suspension polymerization as spherical particles using a monomer mixture which contains a crosslinking agent and an inert diluent. This diluent can be a solvating or nonsolvating solvent for the polymer that is formed, or a soluble polymer or a mixture of polymer and solvent.[2]

In order to obtain a macroporous polymer, a phase separation must occur during the course of the crosslinking process. During the polymerization, the growing polymer becomes insoluble in the reaction medium and precipitates at any stage depending on the inert diluent, that is a poor solvent for the polymer. Thus, the inert diluent acts as a pore-forming agent or porogen and plays an important role in the design of the pore structure of the crosslinked material. The type and amount of porogen used, as well as the degree of crosslinking, temperature and time of polymerization influence the properties and morphology of the polymer.

Macroporous polymers have been mainly synthesized with such water insoluble monomers as acrylates, methacrylates, vinylpyridines, vinylpyrrolidone and vinyl acetate, as well as the widely used styrene-divinylbenze comonomers (St-DVB).[3]

Macroporous polymers have been used as supports for solid-phase extraction (SPE).[4] They have numerous advantages over silica-based sorbents, one of which is that they can be used throughout the pH range because of their hydrolytic stability. Another important characteristic of macroporous supports is that the solvents can access the permanent pore structure and swelling is not critical to accessibility. In SPE, dissolved species are distributed between the sorbent and the liquid phase and the driving force of this process is the interaction of the solute molecules with the sorbent surface. So, a high surface area material that provides good interactions is required. Moreover, when this technique is used to preconcentrate polar analytes, greater surface polarity and hydrophilicity will enhance the sorption properties.

Modifying existing polymers is one possible method of obtaining more polar sorbents. Commercial St-DVB polymers have been modified by introducing acetyl[5], hydroxymethyl[6] and benzoyl moieties.[7] Another method is to copolymerize monomers containing suitable functional groups. Some of these polymers are commercially available: for example, Amberlite XAD-7, which has ester groups; Chromosorb 104, which has nitrile groups, and Oasis HLB, based on N-vinylpyrrolidone/DVB. Macroporous polymers based on acrylonitrile and metacrylonitrile,[8] 2-vinylpyridine[9] and 4-vinylpyridine,[10] in which divinylbenzene is used as crosslinker, have also been described. Other crosslinkers have also been used to prepare macroporous resins, such as vinylpyrrolidone/ethylene dimethacrylate,[11] acrylic acid/ethylene glycol dimethacrylate[12] or methyl methacrylate/ethylene dimethacrylate.[13]

This study explores the preparation of two classes of resins with large surface areas: styrene-divinylbenzene (St-DVB) and 4-vinylpyridine-divinylbenzene (VP-DVB). Different crosslink feed ratios and porogens were investigated and the effect of these variables on the accessible surface area is reported. The sorption properties of these new materials, with different surface areas and nitrogen content, are compared for the solid-phase extraction of polar organic compounds from dilute aqueous solutions.

Experimental

Reagents

Commercial styrene (St), 4-vinylpyridine (VP) and divinylbenzene (DVB) (Aldrich, 80%) were vacuum distilled after washing with a 10% NaOH aqueous solution. The initiators benzoyl peroxide (BPO) and 2,2'-azobisisobutyronitrile (AIBN) were supplied by Aldrich and used as received. Other reagents were used without further purification: toluene (Panreac), dibutyl phthalate (Daesder), methanol (Panreac) and poly(vinylalcohol) (PVA) 23/88 (ERKOL, M. W. 100.000, 88% hydrolized) .

The compounds used to check the sorbents were: phenol (Ph) and 4-nitrophenol (4-NP), both from Aldrich, and oxamyl, N,N-dimethylcarbamoyloxyimino-2-(methylthio)acetamide, and methomyl, S-methyl N-(methylcarbamoyloxy)thioacetimidate, from Riedel-de-Haën . Standard solutions of 2000 mg/l of each compound were prepared in methanol. A mixture of all the compounds used was prepared weekly by diluting the standard solution with Milli-Q water (Millipore), and more dilute working solutions were prepared daily by diluting with Milli-Q. All the solutions were stored at 4ºC in a refrigerator.

HPLC-gradient–grade acetonitrile (SDS) and Milli-Q water were used to prepare the mobile phase. Hydrochloric acid (Probus) was used to adjust the pH of the mobile phase and the sample before SPE to 3.

Polymerization

The polymer beads were obtained by the usual suspension polymerization method in a two-necked round-bottomed flask reactor fitted with a mechanical stirrer and reflux condenser. At room temperature, the flask was charged with the aqueous phase containing 2% PVA. The organic phase —a mixture of styrene or 4-vinylpyridine, divinylbenzene, the diluent system and initiator (1.3 mol. % in relation to the monomer mixture)— was added to the aqueous phase and suspended by stirring. The temperature was kept constant during the reaction period. The specific polymerization conditions are shown in Table 1 and Table 2.

The polymer beads were decanted, washed with water and methanol and dried under vacuum at 40°C. The copolymer was sieved and the fraction in the range of 32-50 μm was selected for SPE evaluation.

Equipment

The surface area of the beads was determined by N_2 adsorption with Micromeritics, ASAP 2000. For VP/DVB copolymers, quantitative C, H and N analyses were performed on a EA1108 Elemental Analyzer CHNS-O (Carlo Erba Instruments) microanalyzer. The IR spectra of the resins were recorded in KBr pellets in the range of 4000-400 cm^{-1} using the Bruker Equinox 55 spectrometer.

The on-line SPE system used to evaluate the sorption properties of the resins consisted of an LC-10AS pump (Shimadzu). This was used to preconcentrate samples through a stainless-steel precolumn (10 x 3 mm I.D.) (Free university, Amsterdam) which had been laboratory packed with the synthesized resins. The extraction system was on-line connected to the chromatographic system by means of a Rheodyne six-port switching valve. The chromatographic system consisted of two LC-10AD_{VP} pumps, an on-line degasser DGU-14a and a CTO-6AS column oven (all from Shimadzu), an injection valve with a 20 μl loop and a HP1100 UV detector (Hewlett Packard). The set-up of the system has been described previously.[14] The chromatographic column was 25.0 cm x 0.46 cm 5 μm Kromasil 100 C_{18} (Teknokroma).

Solid-phase extraction recovery experiments

Before the preconcentration step, the precolumns, which are packed with the synthesized sorbents, were conditioned by flushing with acetonitrile for 2 min at 3 ml/min and activated with 2 ml of Milli-Q water at pH 3 with hydrochloric acid. Then, a selected volume (from 10 to 200 ml) of an aqueous solution of the compounds (adjusted to pH 3 with hydrochloric acid) in a concentration between 20 to 1 μg/l to ensure that the amount of the analyte was constant, was pumped through the cartridge at a flow rate of 3ml/min. Afterwards, the retaining analytes were desorbed and carried on-line to the chromatographic column by the elution solvent (only acetonitrile) in backflush mode.[15] The chromatographic separation was performed at 65ºC and the flow rate was 1 ml/min. The gradient of acetonitrile and Milli-Q water (at pH 3 with hydrochloric acid) was from 20% to 55 % of acetonitrile in 20 min and to 100 % in 5 min. After 2 min the mobile phase returned to the initial conditions in 3 min. The programme of wavelengths for detecting the studied compounds was: first at 240 nm (for detecting oxamyl and methomyl) and at 280 nm after 8 min (for the studied phenolic compounds).

Recovery was calculated from the calibration curve obtained by direct injection.

Results and Discussion

To evaluate the effect of surface area on retention properties, a series of St-DVB sorbents were synthesized using different reaction conditions. Further, a nitrogen-containing monomer, 4-vinylpyridine, was used to test the effect of increasing the polarity of the sorbent.

St- DVB resins

To test how specific surface area affects the sorption capability in solid-phase extraction, several styrene-divinylbenzene resins were synthesized by suspension polymerization. A high specific surface area can be obtained[3] either by choosing inert diluents with the proper solubility parameter or by increasing the amount of inert diluent at the expense of mechanical properties. Alternatively, increasing the amount of the crosslinker in the polymerization mixture increases the specific surface area. Other parameters that can influence the porous structure are the polymerization temperature and the initiator. It has been shown that the size distribution of pores varies significantly with reaction temperature and that increasing temperature shifts the pore size distribution towards smaller pores and increases the specific surface area. [16] Moreover, increasing the decomposition rate of the initiator at a given temperature, also decreases the size of the pores and increases the specific surface area.

Table 1 shows the reaction conditions used in the styrene-divinylbenzene suspension polymerization and their effect on the specific surface area. As can be expected, increasing the amount of crosslinker notably increases the specific surface area of the resins (from 2 m^2/g for St-DVB1 to 552 m^2/g for St-DVB4). Moreover, when the composition of the inert diluent is changed from a mixture of toluene and dibutyl phthalate to pure toluene (St-DVB5) or the reaction time increases (St-DVB6) no significant variations in the specific surface area are observed. Finally, when the reaction temperature was raised to 90°C (St-DVB7), a specific surface area as high as 728 m^2/g was obtained.

Sorption capabilities of St-DVB resins

To evaluate the sorptive properties of the synthesized resins, the on-line solid-phase extraction technique was used with a group of polar compounds (methomyl, oxamyl, phenol and 4-nitrophenol). Different sample volumes (10, 25, 50, 100, 200 ml) of standard solutions (adjusted to pH =3) in an analyte concentration between 20 μg l^{-1} for 10 ml and 1 μg l^{-1} for 200 ml were on-line preconcentrated. Acetonitrile, used as organic solvent in the subsequent chromatographic separation, was used as the elution solvent. Before the organic phase was mixed with the aqueous phase, it eluted the retained analytes in backflush mode. These analytes were then on-line introduced into the chromatographic equipment.

The amount of retained compound should be directly proportional to the available surface area, as most of the polar compounds studied are retained on the surface of the resins as a result of the π-π interactions between the resin and the analyte. Figure 1 shows that, in general, the larger specific surface area, the higher sorption capacity of the resins (St-DVB2, St-DVB3, St-DVB6 and St-DVB7), in terms of the recovery of the compounds, for a given volume (10 ml). However, no significant increases were observed for the higher surface areas.

As an example, figure 2 shows the effect of surface area on the recovery of phenol, which normally presents the lowest interactions with other sorbents in solid-phase extractions [17, 18, 19, 20] , because of its highly polar character.

VP-DVB resins

To improve the adsorption of polar compounds, a more polar monomer such as 4-vinylpyridine has been added to the polymerization mixture. As has been mentioned above, increasing the surface polarity and hydrophilicity while maintaining the capability of allowing π-π interactions will enhance the sorption properties. In spite of the very large quantities of experimental data on the suspension polymerization reported in the literature, there are no exact rules for selecting polymerization conditions and they must be selected for each monomer system. In this way, a study similar to the one described above was carried out and the results are summarized in Table 2.

The presence of vinylpyridine was supported by elemental analysis and by the appearance of a strong absorption at 1597cm^{-1} in the IR spectra, due to the pyridine ring stretching vibrations. As can be seen from the nitrogen content of the resin, the incorporation of the monomer is quantitative for all the compositions of the monomer mixtures.

As in the previous case, increasing the amount of crosslinking monomer (DVB) increases the specific surface area (24 m^2/g for VP-DVB1 to 418 m2/g for VP-DVB4). Since the polarity of the final resin depends on the nitrogen content of the initial mixture of monomers, such reaction parameters as the initiator, the reaction time and the porogen were investigated to increase both the polarity and the specific surface area.

When the initial feed contained a 60% mol of DVB, the introduction of the VP increased slightly when the initiator is AIBN and not BPO (resin VP-DVB5 and VP-DVB4, respectively). The higher the reaction time, the higher the specific surface area (VP-DVB6). Resins VP-DVB7 and VP-DVB8 were obtained by changing the inert diluent. While varying the proportions of toluene and dibutyl phthalate slightly increases the specific surface area, using a mixture of toluene and cyclohexanol, which is a non-solvent for the resin, the specific surface area decreases sharply. Finally, resins VP-DVB9 and VP-DVB10 have the highest specific surface areas for different nitrogen contents and were obtained using pure toluene as inert diluent and a higher amount of DVB in the monomer feed.

Sorption capabilities of VP-DVB resins

Several solid-phase extraction assays, under the same conditions as those followed for the St-DVB resins, were carried out to test the sorption capabilities of the VP-DVB sorbents.

Table 3 shows that the VP-DVB resins that contain a similar quantity of nitrogen (ca. %N = 4.5) and have specific surface areas between 400-500 m^2/g, show no significant changes in their sorptive properties for the range of preconcentrated volumes studied except for phenol. When 100 ml was percolated through the resin VP-DVB4,. the recovery value was lower (49%), although the surface area of this resin (418 m^2/g) was similar to that of the other resins (378 and 495 m^2/g). Therefore, although the specific surface area is involved in the sorption properties of the resin, such parameters as porous volume or particle size also affect the sorptive properties.

When the sorption capabilities of the St-DVB(St-DVB3) resin are compared to those of a VP-DVB resin (VP-DVB4), significant differences are found, although these resins have a similar specific surface area (approximately 400 m^2/g), but the latter have a 4.3 wt. % of nitrogen content in the whole of the polymer. The recovery values are noticeably higher for the most polar compounds (oxamyl, methomyl, phenol and 4-NP) when the polar resin was tested (VP-DVB4) for all the volumes percolated. Figure 3a shows this trend for phenol at a range of percolated volumes between 10 and 200 ml.

A similar effect can be appreciated in figure 3b when the specific surface area was increased up to 700 m^2/g for both series of resins (St-DVB7 and VP-DVB10), even though the nitrogen content of VP-DVB10 is lower (N wt. % = 2.14) than that of VP-DVB4. This indicates much stronger specific interactions (based on the π-π and dipole interactions and hydrogen bonds) between the polar groups in the polymer surface pyridinic group. So, the nitrogen content in the polymer plays an important role in the interaction of the polar analytes. From these results, further work on the synthesis of sorbents with higher specific surface areas and higher nitrogen contents is planned.

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Table 1. Polymerization conditions and properties of poly(Styrene-Divinylbenzene)

RESIN	St-DVB1	St-DVB2	St-DVB3	St-DVB4	St-DVB5	St-DVB6	St-DVB7
Styrene, % molar	80	60	40	20	20	20	20
Divinylbenzene, a% molar	20	40	60	80	80	80	80
Toluene, wt %	88	88	88	88	100	100	100
Dibutyl phthalate, wt %	12	12	12	12	□	□	□
Reaction time (h)	8	8	8	8	8	24	8
Temperature (ºC)	80	80	80	80	80	80	90
Specific surface area (m2/g)b	2	216	438	552	586	547	728

Organic phase/ aqueous phase ratio 1/1; organic phase consisted of: monomer mixture (styrene + divinylbenzene) 33 vol %, porogenic solvent mixture (toluene + dibutylphtalate) 66 vol%, and 1.3 % molar BPO relative to monomers. a Divinylbenzene 80% grade monomer b Specific surface area determined from nitrogen adsorption/desorption isotherm.

Table 2. Polymerization conditions and properties of poly(4-vinylpyridine-Divinylbenzene)

RESIN	VP-DVB1	VP-DVB2	VP-DVB3	VP-DVB4	VP-DVB5	VP-DVB6	VP-DVB7	VP-DVB8	VP-DVB9	VP-DVB10
4-vinylpyridine, % molar	80	60	50	40	40	40	50	50	40	20
Divinylbenzene, a% molar	20	40	50	60	60	60	50	50	60	80

Toluene, wt %	88	88	88	88	88	88	22	88	100	100
Dibutyl phthalate, wt %	12	12	12	12	12	12	78	□	□	□
Ciclohexanol, wt %	□	□	□	□	□	□	□	12	□	□
Initiator (1.3% vs mols monomers)	BPO	BPO	BPO	BPO	AIBN	AIBN	BPO	BPO	AIBN	AIBN
Reaction time (h)	3	3	3	8	8	24	8	8	24	24
N content, b wt %	10.8	7.2	7.0	4.3	4.6	4.6	5.9	5.8	4.5	2.14
N containing monomer incorporation, c% molar	84	59	58	37	39	39	49	48	39	19
Specific surface area (m2/g) d	24	100	115	418	378	495	144	1.21	544	710

Reaction temperature 80 ºC. Organic phase/aqueous phase ratio 1/1; organic phase consisted of: monomer mixture (4-vinylpyridine + divinylbenzene) 33 vol %, porogenic solvent mixture (toluene + dibutylphtalate or ciclohexanol) 66 vol%, and 1.3 % molar BPO or AIBN relative to monomers. a Divinylbenzene 80% grade monomer b Nitrogen content in the polymer determined by elemental analysis c 4-vinylpyridine content in the polymer expresed in molar ratio (%) d Specific surface area determined from nitrogen adsorption/desorption isotherm.

Table 3. Recovery values of studied compounds from 4-vinylpyridine-divinylbenzene resins (VP-DVB4, VP-DVB5, VP-DVB6 and VP-DVB10).

a For the composition and properties of the resins, see table 2.

% Relative standard desviation (R.S.D.) (n =3) were < 6.

Recovery values, %

Resin	VP-DVB4				VP-DVB5				VP-DVB6				VP-DVB10			
Volume (ml)	10	25	50	100	10	25	50	100	10	25	50	100	10	25	50	100
Compounds																
Oxamyl	83	65	30	25	85	57	34	21	85	70	43	26	83	72	70	55
Methomyl	75	48	25	13	83	51	29	16	83	60	34	16	83	69	64	43
Phenol	87	81	75	49	93	93	95	68	87	85	86	70	89	82	83	70
4-NP	81	80	82	81	87	81	81	80	81	81	83	79	83	77	86	85

Figure captions

Figure 1. The dependence of the specific surface area on recovery of the preconcentrated compounds at given volume of 10 ml.

Figure 2. The dependence of the specific surface area on recovery of preconcetrated 4-nitrophenol at a range of volumes from 10 to 200 ml.

Figure 3. Effect of the nitrogen content in the polymer on the recovery values of the phenol at a range of volumes from 10 to 200 ml.
(a) Resins St-DVB3: 438 m2/g (□); VP-DVB4: 418 m2/g and N 4.3 wt.% (□).
(b)Resins St-DVB7: 728 m2/g (□); VP-DVB10: 710 m2/g and N 2.14 wt.% (□).