Synthesis of Davankov-type hypercrosslinked resins using different isomer compositions of vinylbenzylchloride monomer and application in the solid-phase extraction of polar compounds

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Abstract

Two different gel-type resins have been prepared by suspension polymerization using 2wt% divinylbenzene (DVB) with either p-vinylbenzyl chloride (pVBC) or a mixture of VBC isomers (~70% m-; ~30% p-). Significant difference in the chlorine content was observed, which was attributed to a more favoured hydrolysis process when p-VBC was used. The presence of hydroxyl groups has been confirmed by elemental microanalytical data and solid-state ^{13}C cross-polarization/magic angle spinning (CP-MAS) nuclear magnetic resonance (NMR) spectra.

Hypercrosslinked resins were prepared from both gel-type precursors by treatment with $FeCl_3$ in dichloromethane (DCM) at 80 ºC.

The resultant resins showed differences in specific surface area and degree of hydrophilicity. The performance of the hypercrosslinked resins was evaluated in solid-phase extraction (SPE) of polar compounds, and better results were obtained for the hypercrosslinked resin prepared from p-VBC that combines a relatively high specific surface area (908 m^2 g^{-1}) and somewhat higher oxygen content (3.96 wt.% O).

Introduction

Solid phase extraction (SPE) using polymeric resins is a well established method for the extraction of organic pollutants from contaminated water.[1] Conventional polymeric sorbents for SPE applications are crosslinked macromolecular structures mainly based on macroporous styrene-divinylbenzene (St-DVB) resins,[2] which typically display specific surface areas up to ~ 800 m^2 g^{-1}. Since the principal retention mechanism of the polymeric sorbents involves π-π interactions and most polymeric sorbents have a lower than desirable sorption capacity towards many organic compounds, it would seem advantageous to exploit higher surface area resins.[3,4]

Davankov-type hypercrosslinked resins differ from conventional macroporous polymeric sorbents since they are obtained by an extensive post-crosslinking of a preformed linear (or very lightly crosslinked) polystyrene using a bishalide and a Friedel-Crafts catalyst.[4-7] Alternatively, it is possible to use chloromethylated styrene-divinylbenzene (VBC-DVB) copolymers as the starting material in the presence of a solvent and a Friedel-Crafts catalyst.[6,8,9] This converts the chloromethyl groups into methylene bridges so creating new crosslinks additional to those due to the DVB included in the original resin. The resulting structure of the dry hypercrosslinked polymer is an expanded, rigid and three-dimensional network, which displays an extremely high specific surface area (up to 2000 m^2 g^{-1}) and hence excellent sorption properties.[4,7,9-12]

However, despite the large specific surface area, the hydrophobic character of these styrene-based hypercrosslinked resins is not ideally suitable for the sorption of most polar compounds.[11] To overcome the hydrophobicity of the hypercrosslinked polymers some researchers have chemically modified the polymeric matrix by introducing some functional groups.[13-15] However, due to the hypercrosslinked nature of the resin matrix, there tends to be restricted accessibility of the reactive sites, and the degree of modification is generally low, with little improvement of the resin polarity.

Another option is to introduce polarity into the resin via the use of a suitable precursor monomer.[16,17] The choice of an appropriate monomer for the subsequent hypercrosslinking process in not simple because this monomer also has to react in the subsequent Friedel-Crafts reaction. The present study will show that depending on the precursor resin employed (gel-type VBC-DVB, prepared using either p-VBC or mixture of p- and m- isomers) the hypercrosslinked materials synthesized have different degrees of hydrophilicity and specific surface area. These features have been profitably exploited in the SPE of three topical polar phenolic compounds.

Experimental

Materials

Divinylbenzene (DVB), was the ~80% technical grade quoted as an 80% mixture of 1,3- and 1,4-DVB isomers and 20% 1,3- and 1,4-ethylstyrene isomers and supplied from Aldrich Chemical Co. It was purified by passing through a silica column. p-Vinylbenzylchloride (pVBC) was a 95% technical grade and the mixture of isomers vinylbenzyl chloride (mixVBC) was 97% technical grade quoted as 30% p-VBC and 70% m-VBC. Both were used as supplied from Dow Chemical Co. The azobisisobutyronitrile (AIBN) used as a initiator was purified by recrystallization from acetone and supplied from BDH Chemical Co. The stabilizer Mowiol® 40-88 (PVA, 88% hydrolyzed, Mw ~127.000) was from the Aldrich Chemical Co. and sodium chloride from the Fluka Chemical Co.. Ferric chloride, 97% and 1,2-dichloroethane (DCE) anhydrous 99,8%, both from Aldrich Chemical Co., were used in the hypercrosslinking reactions.

The phenolic compounds used in the SPE experiments were: resorcinol, phenol and 4-nitrophenol, all supplied from the Aldrich Chemical Co. Standard solutions of 2000 mg l^{-1} of each compound were prepared in methanol. A mixture of all compounds was prepared by diluting the standard solution with Milli-Q water (Millipore).

HPLC–grade acetonitrile (SDS) and Milli-Q water were used to prepare the mobile phase to test each sorbent by HPLC. Before SPE hydrochloric acid (Probus) was used to adjust the pH of the mobile phase and the sample to 3.

Suspension polymerization synthesis of the gel-type resins 2%wtDVB-98%wtVBC

The gel-type resins were obtained by suspension polymerization.[8] A measured volume (700 ml) of the aqueous phase (7.5 g Mowiol ® and 33 g NaCl in 1000 ml water) was poured into a baffled 1000 ml suspension polymerization reactor fitted with a water condenser and mechanical stirrer carrying a double impeller. The organic phase containing DVB (0.7998 g; $6.15 \cdot 10^{-3}$ mol), mixVBC or p-VBC (39.102 g; 0.256 mol) and 0.5 wt% AIBN (0.1995 g; $1.21 \cdot 10^{-3}$ mol), was mixed and maintained for 30 minutes under nitrogen; then it was suspended as spherical droplets in the aqueous phase (in a ratio of 20:1 of aqueous phase: organic phase) by stirring at 425 rpm. The suspension was maintained under nitrogen at 80ºC for 6 hours.

The product beads were washed with water on a sieve (75 μm) and then with methanol. After further washing with water and methanol, the resin was placed in a Soxlhet apparatus and extracted with acetone overnight to eliminate the remaining impurities. Finally the resin was washed with methanol and diethyl ether in a filter funnel and dried in a vacuum oven for a day at 40 ºC.

The resulting beads were then size fractionated using sieves, and the fraction between 106 and 212 μm was used in all the experiments.

Synthesis of the hypercrosslinked resins derived from gel-type precursors

The hypercrosslinked resins were obtained using the following optimized synthetic method.[8] The gel-type resin (2.5 g) (2%DVB-98%VBC) was placed in a water-jacked round bottomed flask (100 ml) and DCE (40 ml) added to the polymer. The solution was left under nitrogen for 1 hour to swell the beads. Then ferric chloride (in a molar ratio 1:1 of CH_2Cl: $FeCl_3$) in DCE (40 ml) was added to the suspension of resin beads. The final mixture was heated rapidly to 80 ºC and kept at this temperature for 18 hours.

The beads were then washed as previously described for the gel-type resins.

Equipment

***Elemental Analysis*.** Elemental microanalytical data (%C, %H, %Cl and %O) for the resins were obtained from a Carlo-Erba EA1106 instrument. The chlorine content was determined using Schöninger's method [18], which involves the combustion of the sample in a closed platinum vessel and the potentiometric measurement of the HCl evolved. The oxygen content was determined using Unterzaucher's method [19] in the presence of activate carbon and under an inert atmosphere.

Fourier transform infrared spectra (FTIR). The ATR mode FTIR spectra were recorded using a Jasco FT/IR – 680 Plus Spectrometer.

***N_2 Sorption Porosimetry*.** N_2 sorption isotherms were generated using a Micromeritics ASAP 2010 instrument. The package software was used to compute resin surface areas from the adsorption branch of the isotherm using the BET model.

NMR Spectrometry. Solid-state ^{13}C CP/MAS (cross polarization magic angle spinning) NMR spectra were recorded on a Varian Mercury Vx 400 MHz solid-state NMR spectrometer operating at 118 MHz. Samples were finely powdered, and packed into a 7 mm rotor. The samples were spun at 5.0 kHz at room temperature. Hexamethylbenzene was used as an external standard.

SPE-HPLC. The on-line SPE system used to evaluate the sorption properties of the resins, consisted of an LC-10AS pump (Shimadzu), which was used to preconcentrate samples through a stainless-steel precolumn (10 x 3 mm I.D.) (Free University, Amsterdam) packed in-house 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, a CTO-6AS column oven (all from Shimadzu), an injection valve with 20 μl loop and a HP1100 UV detector (Hewlett Packard). The chromatographic column was 25.0 x 0.46 cm 5 μm Kromasil 100 C_{18} (Teknokroma).

Solid-phase extraction recovery experiments

Before the preconcentration step, the precolumns were packed with the synthesized sorbents in a 50-75 μm particle size, which is more suitable for packing and which was obtained by crushing the original particles (106-212 μm). The sorbents were conditioned by flushing with acetonitrile for 2 min at 3 ml min^{-1} and activated with 2 ml of Milli-Q water at pH 3 with hydrochloric acid. Then, a selected volume (from 10 to 300 ml) of Milli-Q water at pH 3 (HCl) with a mixture of the three phenolic compounds, in a concentration between 20 to 0.6 μg l^{-1} depending on the volume, was pumped through a cartridge, at a flow rate 3 ml min^{-1}. Afterwards, the retained analytes were desorbed and transferred on-line to the chromatographic column by the elution solvent (neat acetonitrile) in backflush mode. The chromatographic separation was performed at 65ºC and the flow rate was 1 ml min^{-1} using initially a solvent gradient of acetonitrile in acidified Milli-Q water at pH 3 (HCl) from 15% to 20 % in 10 min, 50% at 20 min and 100 % solvent at 30 min (held for 2 min), after which the mobile phase was returned to the initial conditions in 3 min. The phenolic compounds studied were detected at 280 nm.

Analyte recovery was calculated from the calibration curve obtained by direct injection.

Results and discussion

The synthesis and application of hypercrosslinked styrenic resins prepared from VBC precursor resins have been reported in earlier studies,[3,8] but none of these have focused on which VBC isomers are used in the synthesis of the precursor resins and the compositional differences that arise, and indeed how these differences are manifest in resin application.

Synthesis of the gel-type resins

Two gel-type (2wt%DVB-98wt%VBC) precursor resins were synthesized using exactly the same suspension polymerization conditions and changing only the VBC isomer composition used. The first gel-type resin (GpVBC-DVB) was synthesized using p-VBC as functional monomer and the second one (GmixVBC-DVB) consisting of mixture of isomers (~30% p- and ~70% m-).

The elemental microanalytical data for these resins are detailed in Table 1, where it is clear that the resin prepared from p-VBC (GpVBC-DVB) has significantly lower chlorine content (8.42 wt.%Cl) than theoretical (20.85 wt.%Cl), whereas the %C and %H values are very close to the theoretical values. This suggests that another element is likely to be present in the structure. Examining the elemental microanalytical data results for the resin prepared from mix-VBC (GmixVBC-DVB), it can be seen that the chlorine content is noticeably higher (18.71 wt.%Cl) with respect to the values obtained for the GpVBC-DVB resin (8.42 wt.%Cl), and much closer to the theoretical value (20.85 wt.%Cl).

The low chlorine content in the resin synthesized from p-VBC (GpVBC-DVB) might be explained by the favoured hydrolysis of the chloromethyl group in the position para to the vinyl group in p-DVB. Hydrolysis of benzyl chorides might be expected to proceed via an SN_1 mechanism involving the generation of the corresponding stabilized carbocation intermediates, and followed by nucleophilic attach of water. Suspension polymerizations are carried out at elevated temperature in the presence of excess water and it is not therefore surprising that this side reaction occurs. Furthermore the carbocation derived from p-VBC would be expected to be more stabilized than that derived from m-VBC because of contributions from 5 canonical structures versus 4 (Figure 1). The carbocation from p-VBC would therefore form more readily and hence the hydrolysis of p-VBC would be expected to proceed more rapidly than that of m-VBC. This seems to be the most likely explanation for the significant loss of chlorine during the synthesis of gel-type resin GpVBC-DVB. If this is so resin GpVBC-DVB might be expected to have a significant content of OH groups.

Indeed, the presence of oxygen in the resin was confirmed by direct oxygen microanalysis (Table 1). The %O content in GpVBC-DVB resin (8.16 wt.%O) is higher than the %O content in GmixVBC-DVB (2.92 wt.%O). Moreover, the small content of oxygen (2.92 wt.%O) in resin GmixVBC-DVB confirms that the para isomer is more rapidly hydrolysed since the mixed VBC contains only

~30% p-isomer. This also suggests that a resin prepared from 100% m-VBC would have even higher hydrolytic stability.

Identification of hydroxyl groups

Although the microanalytical data supports the presence of oxygen, the hydrolysis process and the presence of hydroxyl groups in the gel-type precursor resins should be detectable spectroscopically. Indeed the presence of hydroxyl groups in the resin was confirmed first in the FTIR spectrum by a band ~3400 cm^{-1} which is much larger in the GpVBC-DVB spectrum (Fig. 2a) than in the GmixVBC-DVB spectrum (Fig. 2b). Another feature of the spectra is the presence of the sharp band at 1265 cm^{-1} which is characteristic of the CH_2Cl group. In the resin GmixVBC-DVB (fig. 2b) this peak is larger than in the hydrolyzed resin GpVBC-DVB (fig.2a); again this is consistent with the lower Cl content in GpVBC-DVB.

Solid-state ^{13}C NMR was also used to verify the presence of hydroxyl moieties in the resins. Figure 3 shows the solid-state ^{13}C NMR spectra acquired with cross polarization magic angle spinning (CP/MAS) at 5kHz. In the NMR spectrum of GpVBC-DVB (Fig. 3a) there is a resonance at 64.92 ppm, which is characteristic of the hydroxymethyl carbon. There are also two overlapping resonances, one at 46.75 ppm, which is assigned to the chloromethyl carbon, and another peak at 40.24 ppm, corresponding to polymer backbone methylene-methine carbons.[5,20] In the NMR spectrum of GmixVBC-DVB (Fig. 3b) these resonances are also visible, but some differences should be noticed. Firstly, the hydroxymethyl resonance at 65.19 ppm can hardly be seen, confirming the low content of OH groups in resin GmixVBC-DVB. Moreover, with the overlapping resonances, at 46.91 and 40.44 ppm, the former chloromethyl peak is more intense than the latter methylene-methine peak. This is not the case in the ^{13}C NMR spectrum (Fig. 3a) of the resin GpVBC-DVB. This last observation is in concordance with the higher chlorine content in GmixVBC-DVB resin than in the GpVBC-DVB resin.

Thus, from both the FTIR and NMR spectroscopic results we can attribute the oxygen content obtained from the elemental analytical data substantially to hydroxyl groups in the resins.

Synthesis of the hypercrosslinked resins from the gel-type resins

The degree of hypercrosslinking of chloromethylated polystyrene precursor resins achieved on treatment with Lewis acids is mainly a function of the Cl content, but also to some extent of the morphological properties of the precursor resin. Gel-type resins might be expected to be the most appropriate precursor, because such resins are more easily swollen than macroporous ones and, therefore, should provide better access for crosslinking.[7,8] In the present study two gel-type resins were examined as precursors: one with rather low chlorine content: GpVBC-DVB (8.42 wt.%Cl) and one with a much higher chlorine content: GmixVBC-DVB (18.71 wt.%Cl). Indeed the former resin might be regarded as possessing too low a level of chloromehyl groups to generate a hypercrosslinked network, but this species also contains a balancing level of hydroxymethyl groups as a result of the in-situ hydrolysis reaction during the synthesis. In simplistic terms it might be expected that the higher the chlorine content, the higher the crosslinking degree and the higher the specific surface area. Therefore, resin GmixVBC-DVB might be expected to yield a hypercrosslinked resin with a larger specific surface area. On the other hand, the presence of the hydroxyl moieties in resin GpVBC-DVB, due to the hydrolysis process, might allow the production of a hypercrosslinked resin with some residual hydroxyl (polar) groups, which would be interesting in terms of their potential retention capabilities. Hypercrosslinking of both resins (GpVBC-DVB and GmixVBC-DVB) was therefore pursued.

Table 2 summarizes the characterization data obtained for the hypercrosslinked resins. The Cl content (indicative of the methylene bridging) falls in 18 hours from 8.42 to 2.81 wt.% for HXLGp and from 18.71 to 6.03 wt.% for HXLGmix. The consumption of the -CH_2Cl groups is confirmed in FTIR spectra (Fig. 4), in which the 1265 cm^{-1} peak all but disappears. This is seen most clear in comparing the spectrum of resin HLXGmix (Fig. 4b) with that of the resin GmixVBC-DVB (Fig. 2b).

The specific surface areas of the hypercrosslinked resins are also shown in Table 2. As expected the higher the Cl content of the precursor resin, the higher the specific surface area generated in the corresponding hypercrosslinked resin. Thus, resin HXLGmix has a higher specific surface area of 1889 m^2 g^{-1} and that of resin HXLGp is 908 m^2 g^{-1}.

Another remarkable feature of the characterization data is the substantial fall in the oxygen content of the precursor resin GpVBC-DVB (8.16 wt.%) when subjected to the hypercrosslinking reaction to form resin HXLGp (3.96 wt.%). Indeed if all the hydroxyl groups were to be retained during this reaction, the loss of chlorine content (from –CH_2Cl) in forming methylene bridges would result in an increase in the wt.% of all the other elements including the oxygen. The ~50% fall in the oxygen content, therefore indicates a loss of some of the hydroxyl groups, and this is confirmed by the large decline in the intensity of the broad OH stretching band in the FTIR spectra at ~3460 cm^{-1} (Figures 2a and 4a). Similar but less substantial changes are seen in the FTIR spectra of the precursor resin GmixVBC-DVB and its corresponding hypercrosslinked derivative resin HXLGmix (Figure 2b and 4b). It does seem conclusive therefore that the hydroxymethyl groups do participate in the methylene bridging reaction along with the chloromethyl groups and indeed in organic synthetic terms this is not unreasonable. Two mechanisms can be envisaged. Firstly, the anhydrous Lewis acid, $FeCl_3$, might chlorinate the hydroxymethyl groups and hence increase the level of chloromethyl groups present. Secondly, the oxygen atom of hydroxyl groups might coordinate to a powerful Lewis acid such as anhydrous $FeCl_3$, hence activating the hydroxyl group as a leaving group and facilitating its participation in methylene bridging. The involvement of hydroxymethyl groups by one or indeed both of these mechanisms also explains the formation of a resin (HXLGp) with a surface area as high as 908 m^2 g^{-1} when the original chlorine content in the precursor resin (GpVBC-DVB) was only 8.42 wt.%. It is of course very difficult to quantify the level of crosslinking in the resin HXLGp (and indeed in HXLGmix) but for the present work the important result is that high surface area resins are formed from both precursor gel-type resins. Both contain significant levels of hydroxyl groups, and that to some extent there is a balance between the hydroxyl group content and the surface area. Intriguingly therefore it seems that with the appropriate choice of the VBC isomer composition used in the synthesis of the precursor gel-type resin, it is possible to control both the surface area and the degree of hydrophilicity of the derived hypercrosslinked resin.

Sorption behaviour of the hypercrosslinked resins

Resins HXLGp and HXLGmix have been used as sorbents in the on-line SPE for a group of polar compounds. For this purpose, a precolumn was packed with the synthesized hypercrosslinked resin (~ 40 mg) (50-75 μm) and, after the conditioning step, different sample volumes (10-300 ml) spiked (20 to 0.6 μg l^{-1}) with a mixture of the three selected polar compounds (resorcinol, phenol and 4-nitrophenol) were passed through the precolumn. Afterwards, the trapped analytes were desorbed and transferred on-line to a chromatographic column by the elution solvent (acetonitrile) in backflush mode.

Although there are a number of published studies where the retention properties of hypercrosslinked resins have been evaluated,[11,21-23] it should be pointed out that the method used in the present study has not been used previously. The approach used here is pertinent to the analysis of e.g. environmental samples and has been adopted to allow the facile transfer to the analysis of real samples where similar analyte concentrations arise.

The recoveries for the phenolic compounds are compared in Figure 5. As a general rule, the attraction between a hydrophobic sorbent (i.e. HXLGmix) and a polar analyte arises only via π-π interactions, whereas the attraction between a hydrophilic sorbent (i.e. HXLGp) and a polar analyte can arise from a combination of hydrogen bonding, dipole-dipole interactions and also π-π interactions.[4] The present results show that a higher retention by HXLGp can be achieved for the volumes up to 100 ml of percolated resorcinol solution (Figure 5 a), but for larger volumes of sample, resorcinol is poorly retained by both sorbents due to its high polarity. Phenol (Figure 5b) also shows greater recoveries using HXLGp, and the highest differences arise for 200 and 300 ml of percolated solution. For instance, the recovery from 300 ml of percolated phenol solution when HXLGp is used as sorbent is 72%, whereas when HXLGmix is used the recovery down to 33%. The above trend is not seen with 4-nitrophenol (Figure 5c). The nitro group acts as strong electron withdrawing group in reducing the overall electron density in the benzene ring and this enables the nitrophenol to form a stronger donor-acceptor adduct [11,24] than the rest of the phenolic compounds with electron rich aromatic groups in both HXLGp and HXLGmix. Thus, 4-nitrophenol has a similarly high recovery with both of the hypercrosslinked sorbents.

Another important point in the SPE results is that the new hypercrosslinked resins allow percolation by on-line SPE samples volumes as high as 300 ml, whereas the largest volumes that can usually be employed without losses of polar compounds such as phenol by on-line SPE are rarely higher than 100 ml using normal pre-column sizes.[25] The new hypercrosslinked resins therefore have very good capacity.

In order to compare the behaviour of our new resins, some commercially available materials were tested under the same conditions. The selected resins were Amberchrom GC-161m [26] (hypercrosslinked St-DVB resin, specific surface area 900 m^2 g^{-1}, Tosohaas, PA, USA), Lichrolut EN (hypercrosslinked St-DVB resin, specific surface area 1200 m^2 g^{-1}, Merk, Darmstadt, Germany) [27] and macroporous St-DVB (728 m^2 g^{-1}, previously synthesized by our group [16]).

Figure 6 shows the recoveries from different volumes of sample spiked with phenol. From the plots it is clear that the conventional macroporous resin (St-DVB) shows much poorer retention than all the hypercrosslinked resins, despite of the fact that its specific surface area (728 m^2 g^{-1}) is quite similar to that of the hypercrosslinked resins, Amberchrom GC-161m and HXLGp (~900 m^2 g^{-1}). As for the hypercrosslinked resins, the larger the specific surface area, the higher the recoveries, consequently the trend in the recoveries are:

Amberchrom (900 m^2 g^{-1}) < Lichrolut EN (1200 m^2 g^{-1}) < HXLGmix (1889 m^2 g^{-1})

However, as pointed from the data in Figure 5, the optimal resin for phenol recovery is the hydrophilic hypercrosslinked resin HXLGp with a surface area of 908 m^2 g^{-1}.

Conclusions

Differences in the synthesis of gel-type resins (2 wt.% DVB – 98 wt.% VBC) using different VBC isomers are attributed to the more favoured in-situ hydrolysis of pVBC relative to mVBC during suspension polymerization. The presence of hydroxyl groups in these gel-type resins was confirmed by elemental analysis and FTIR and solid-state ^{13}C NMR spectroscopy.

The subsequent hypercrosslinked resins prepared from the above precursors show differences in the specific surface area and oxygen content and hence hydrophilicity, according to the gel-type precursor used in their synthesis. Thus, it is possible to control the degree of hydrophilicity and specific surface area of SPE sorbents, by defining the feed ratio of the isomeric VBC monomers used in their synthesis.

Evaluation of the retention properties of these hypercrosslinked resins in SPE of polar phenolic compounds shows that, recoveries are higher for the resin with good surface area (~900 m^2 g^{-1}) but also with significant hydroxyl group content.

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Table 1. Elemental microanalytical data for the gel-type resins

	theoretical	experimental	
		GpVBC-DVB **from pVBC**	**GmixVBC-DVB** **from mixVBC**
wt.% C	73.05	76.11	71.92
wt.% H	6.09	7.30	6.26
wt.% Cl	20.85	8.42	18.71
wt.% O		8.16	2.92

Table 2. Hypercrosslinked resin characterization data

	HXLGp **from GpVBC-DVB**	**HXLGmix** **from GmixVBC-DVB**
wt.% Cl [a]	2.13	5.34
Cl loading (mmol g^{-1})	0.60	1.50
wt.% O [a]	3.96	2.5
OH loading (mmol g^{-1})	2.35	1.47
BET surface area (m^2 g^{-1}) [b]	908	1889

[a] Determined by direct elemental analysis.

[b] Determined from adsorption arm of N_2 sorption isotherms.

Figure captions.

Figure 1. Canonical structures of carbocations derived from p- and m-DVB.

Figure 2. FTIR spectra of GpVBC-DVB (a) and GmixVBC-DVB (b).

Figure 3. Solid-state (118 MHz) ^{13}C CP/MAS NMR spectra of GpVBC-DVB (a) and GmixVBC-DVB (b). Spinning speed was 5 kHz. Spinning side bands are indicated by *.

Figure 4. FTIR spectra of HXLGp (a) and HXLGmix (b).

Figure 5. Comparison of the analyte recoveries using HXLGp (▲) (specific surface area = 908 $m^2\ g^{-1}$; 3.96 wt.%O) and HXLGmix (♦) (specific surface area = 1889 $m^2\ g^{-1}$; 2.50 wt.%O) at volumes of 10-300 ml for a) resorcinol, b) phenol and c) 4-nitrophenol.

Figure 6. Comparison of phenol recoveries for different volumes of spiked sample using different resins: HXLGp (▲) (908 $m^2\ g^{-1}$); HXLGmix (♦) (1889 $m^2\ g^{-1}$); Amberchrom GC-161m (×) (900 $m^2\ g^{-1}$); Lichrolut EN (▪) (1200 $m^2\ g^{-1}$); macroporous St-DVB (●) (728 $m^2\ g^{-1}$).

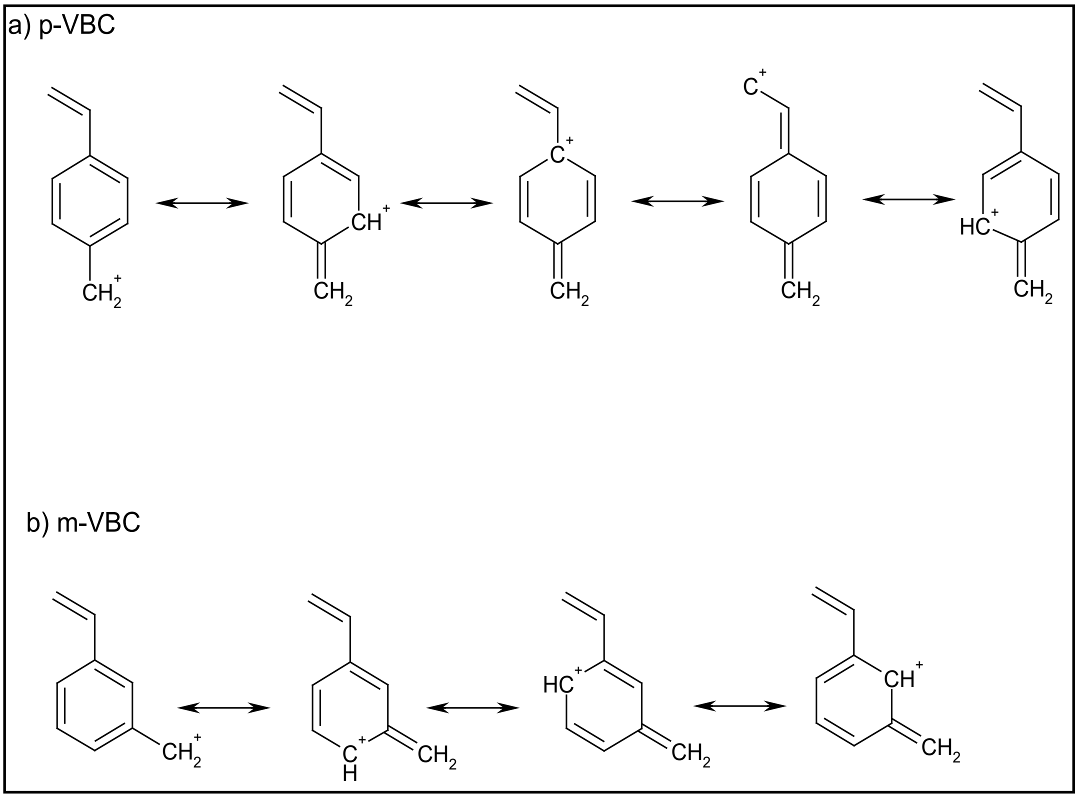

Figure 1

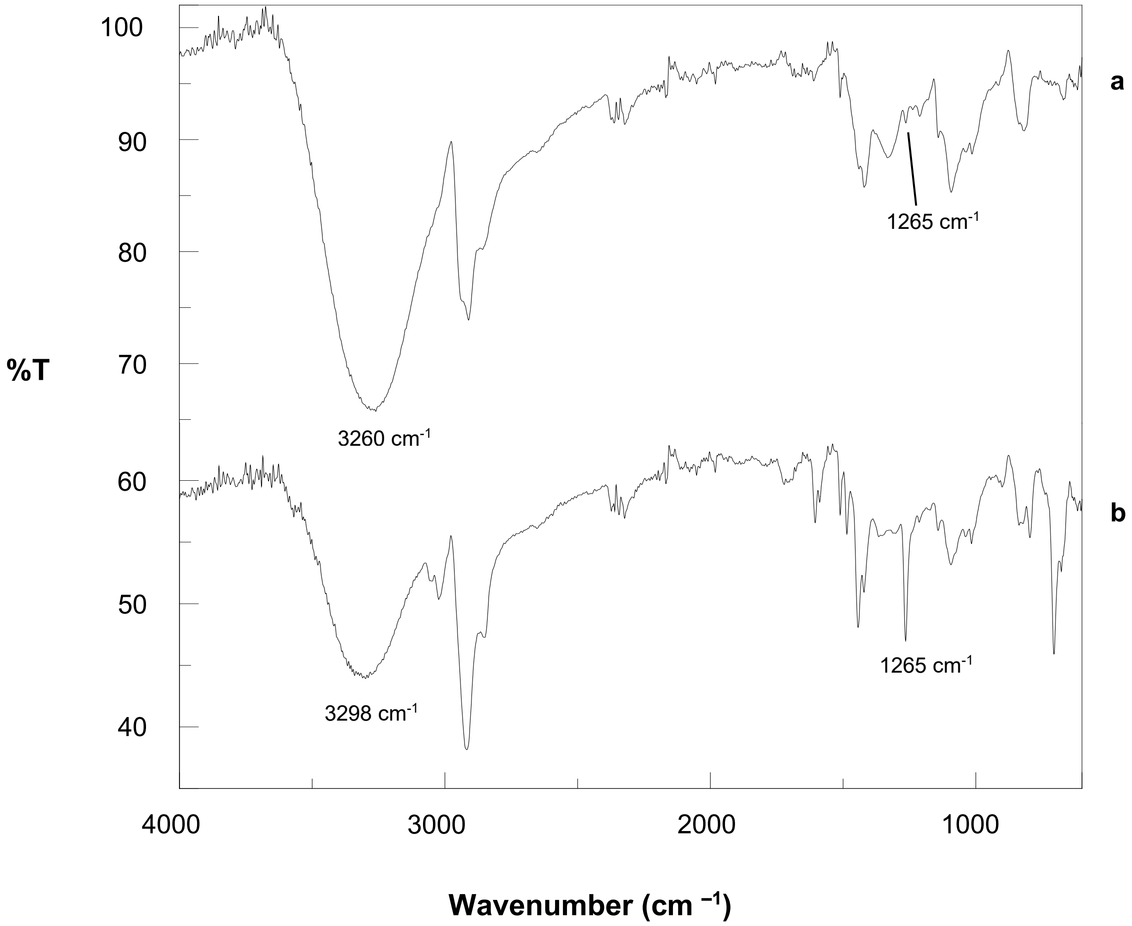
100
90
80
70
60
50
40
%T
4000
3000
2000
1000
Wavenumber (cm $^{-1}$)
a
b
3260 cm^{-1}
1265 cm^{-1}
3298 cm^{-1}
1265 cm^{-1}

Figure 2

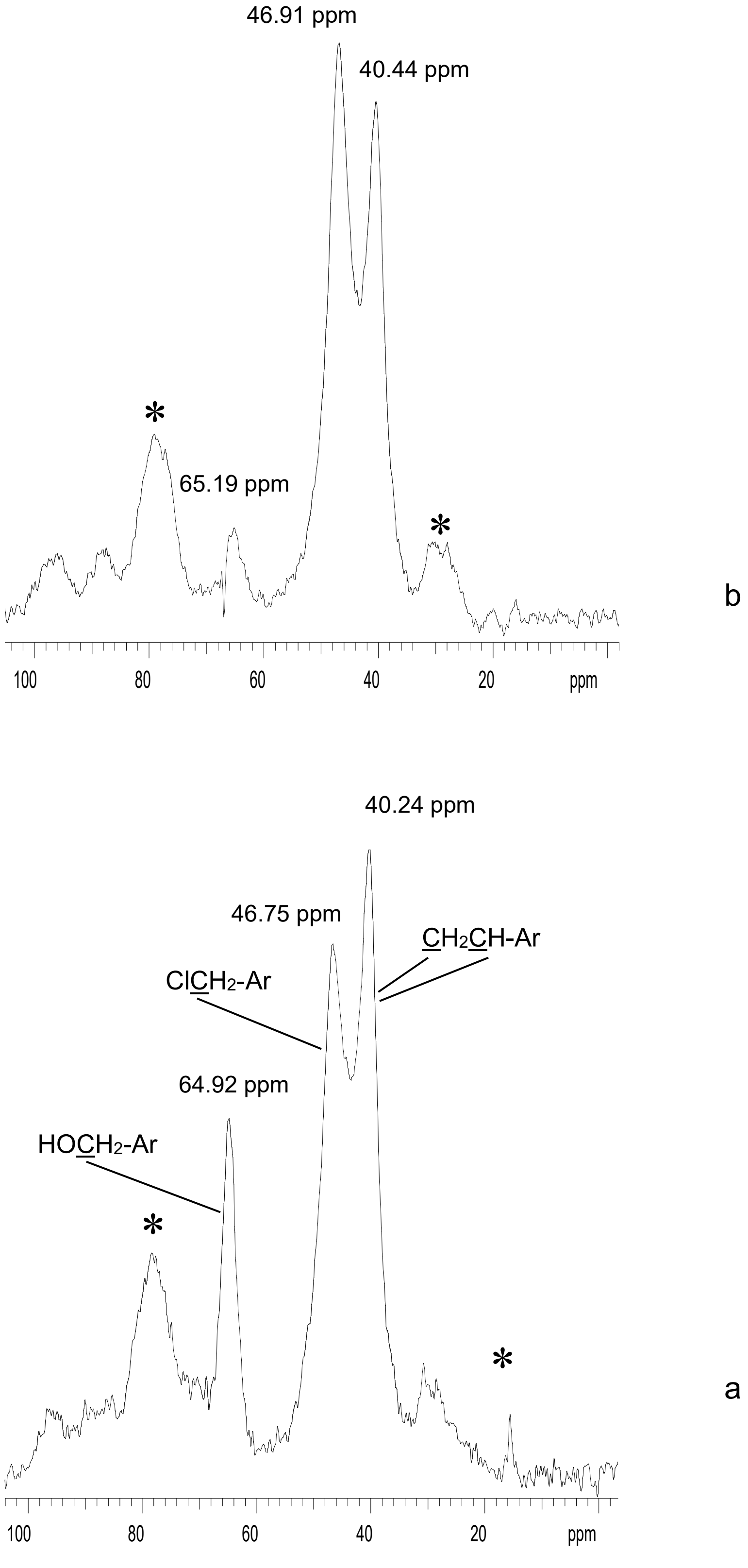
46.91 ppm
40.44 ppm
*
65.19 ppm
*
b
100
80
60
40
20
ppm
40.24 ppm
46.75 ppm
$\underline{C}H_2\underline{C}H$-Ar
$Cl\underline{C}H_2$-Ar
64.92 ppm
$HO\underline{C}H_2$-Ar
*
*
a
100
80
60
40
20
ppm

Figure 3

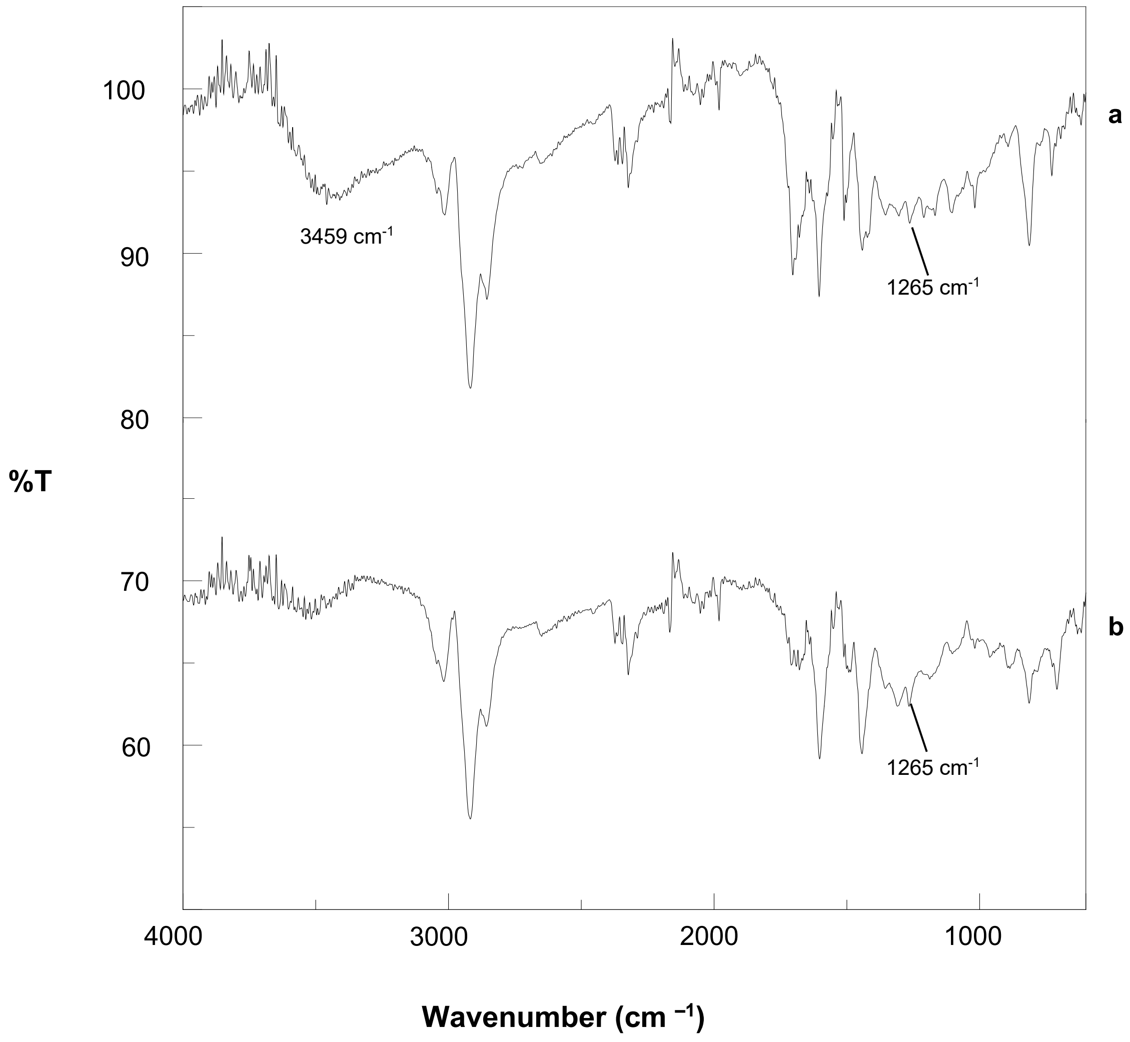
100
90
80
70
60
%T
4000
3000
2000
1000
Wavenumber (cm −1)
a
b
3459 cm-1
1265 cm-1
1265 cm-1

Figure 4

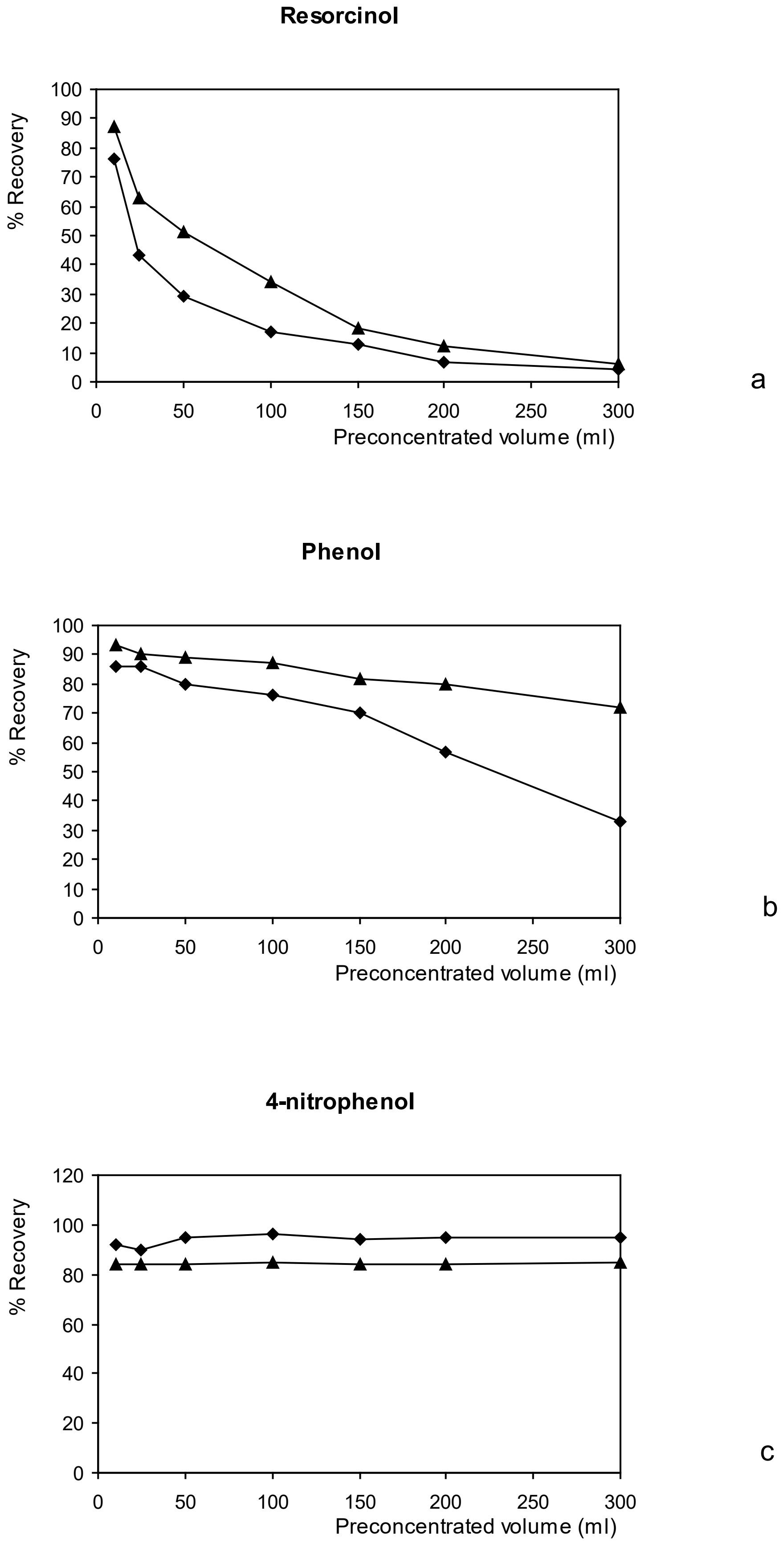
Resorcinol
% Recovery
0
10
20
30
40
50
60
70
80
90
100
0
50
100
150
200
250
300
Preconcentrated volume (ml)
a
Phenol
% Recovery
0
10
20
30
40
50
60
70
80
90
100
0
50
100
150
200
250
300
Preconcentrated volume (ml)
b
4-nitrophenol
% Recovery
0
20
40
60
80
100
120
0
50
100
150
200
250
300
Preconcentrated volume (ml)
c

Figure 5

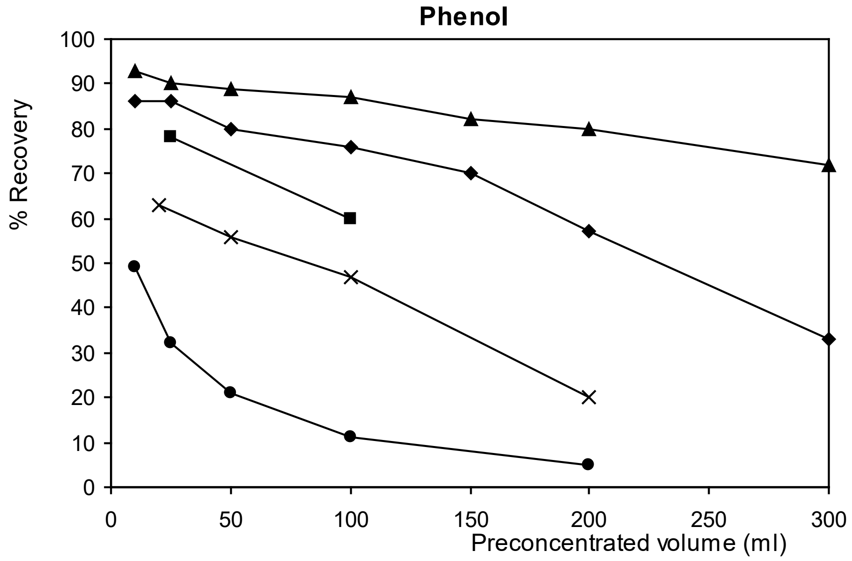
Phenol
% Recovery
Preconcentrated volume (ml)
0
10
20
30
40
50
60
70
80
90
100
0
50
100
150
200
250
300

Figure 6