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Synthesis of a poly(vinylcatechol-co-divinylbenzene) resin and accessibility to catechol units

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ABSTRACT

Poly(vinylcatechol-*co*-divinylbenzene) resins have been prepared by suspension copolymerization of 3,4-dimethoxystyrene (DMS) with divinylbenzene (DVB) using toluene as the porogen and followed by deprotection of the catechol functions. The ratio of DMS versus DVB was modified and led to a maximum catechol content (determined by elemental analysis) varying from 0.82 to 3.16 mmol g^{-1}. Large surface areas were found for copolymers prepared with a divinylbenzene content larger than 35% v/v: from 464 to 658 $m^2 g^{-1}$. Accessibility (determined by back titration of the hydroxyl groups) was improved by prior contact with ethanol but remained inferior to 20%. This can be the result of the morphology of the resin beads and of the bottle-shape form of the pores, or/and of the embedding of the catechol units inside the polymer network. The sorption capacities were determined for Cu(II) and Cd(II) and reached 101.5 and 81.0 μmol g^{-1} for copper and cadmium, respectively. Moreover, a significant variation of coloration has been observed upon complexation of copper by the resins.

1. Introduction

Crosslinked porous copolymers have been widely developed over the past decades because of their numerous applications in many areas including ion exchangers, chromatographic packings, polymer-supported catalysts, solid-phase extraction adsorbents, etc. [1–5]. In particular, much attention has been paid to macroporous poly(styrene-*co*-divinylbenzene) particles and to the control of their porosity. The term "macroporous" is not in agreement with the IUPAC nomenclature (macropores > 50 nm diameter) [6] but refers to resins possessing a permanent pore structure in opposition with "gel-type resins". The polymer beads are prepared by suspension copolymerization in water in the presence of a porogen that can be either a diluent, an oligomer or a polymer. The phase separation induced by this porogen during the copolymerization process is responsible for the formation of the pores [7]. The morphology of the final resins depends on the kind and amount of porogen and also on the degree of crosslinking [8].

Many applications require the chemical modification of the resins surface. This can be classically achieved by post synthesis grafting of functional groups that may be introduced with a reactive precursor such as an amine or a chloromethyl group [9,10]. An alternative is to directly incorporate the functional group through copolymerization of an appropriate monomer. This is more convenient to perform because of the lower number of synthetic steps and the better reproducibility [11]. However, the formation of the pore structure can be affected by the replacement of styrene by a functional monomer because of the possible modification of reactivity [12,13]. Therefore, the copolymerization experimental parameters (type and amount of the diluent, crosslinker concentration…) must be adapted to this modification.

The efficiency of these macroporous resins, in their diverse uses, is linked to their sorption capacity and to the accessibility of their active functions. Obviously, the most accessible groups are on the outer surface of the particles. But this corresponds to an extremely low capacity and therefore a control of the pore accessibility is required to improve it. Nevertheless, a too large increase in surface area might not be efficient if the pore size becomes too small and prevents their access [14]. In the field of catalysis, it has been shown that large pores, even leading to small surface area, can be efficient since they prevent diffusion problems [15]. As far as diffusion is concerned, accessibility

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of the active groups depends not only on consolidated pores structure and size but also on the extent of swelling and its morphology [16]. Depending on the desired application, a compromise must be found between capacity and accessibility.

Here, we report the preparation of a macroporous resin containing catechol (1,2-dihydroxybenzene) as an active function. Catechol has proved to be a remarkable versatile agent in organic chemistry with low redox potentials, high reactivity toward electrophilic aromatic substitution and coplanar bidentate complexing properties [17]. Its copolymerization requires the use of a protected form since it is an inhibitor of polymerization. Therefore, commercial 3,4-dimethoxystyrene (DMS) was used as a functional monomer to prepare a porous resin in which accessible groups are further deprotected in a second step to recover the hydroxyl groups. Although the copolymerization of DMS with styrene has already been described to give poly(vinylcatechol-*co*-styrene) [18], the synthesis of poly(vinylcatechol-*co*-divinylbenzene) has not yet been published. For this purpose, spherical beads were prepared by suspension copolymerization. The pore structure of these resins was studied and correlated to the accessibility of the catechol functions by hydroxide, Cu(II) and Cd(II) ions.

2. Experimental section

2.1. Materials

Divinylbenzene (DVB) (80% technical grade), styrene (>99%), 3,4-dimethoxystyrene (DMS) (technical grade), azobis(isobutyronitrile) (AIBN) and NaCl were supplied by Sigma Aldrich. Polyvinylalcohol (PVA, 88% hydrolysed, Mw ~ 8800 g mol^{-1}), toluene, acetone, ethanol, dichloromethane, boron tribromide, NaOH and HCl 37% were from Acrös Organics.

For the determination of complexing properties, Cu(II) and Cd (II) solutions (1 g L^{-1}) from Panreac and HNO_3 suprapure 65% from Carlo Erba were used. All metal solutions were prepared with ultra-high quality deionized water (Millipore, resistivity > 18 mΩ cm).

2.2. General synthetic process for DVB–St and DVB–DMS copolymers

Polymerization was carried out in a 250 mL round-bottomed flask under mechanical agitation (200 rpm). The PTFE stirrer blade dimensions were: 14 × 50 mm (double articulated-paddle) and the shaft diameter 8 mm. A total of 0.4 g of PVA were dissolved in 80 mL of deionized water at 80 °C for 4 h then 0.4 g (6.8 mmol) of NaCl were introduced and the reaction mixture was placed under nitrogen atmosphere (purge of 15 min). Prior to polymerization, the mixture of monomers was extracted with 10% NaOH solution and rinsed with ultra pure water. The composition of the organic phase containing monomers and toluene (total volume of 20 mL) is given in Table 1. After addition of 0.1 g (6.1 mmol) of AIBN to the organic mixture, it was introduced in the polymerization flask under nitrogen atmosphere. The polymerization was run at 80 °C for 6 h. The resin beads were collected by filtration and washed with hot water. They were then extracted in a Soxhlet 24 h with water and 24 h with ethanol and then dried under vacuum for 3 days at room temperature. Conversion rates vary from 90 to 98%. Beads were sieved between 300 μm and 700 μm: 99% of the resin beads have a diameter between 300 and 700 μm.

2.3. Synthesis of DVB–DOH copolymers

A total of 3.5 g of DVB–DMS were suspended in 50 mL of anhydrous dichloromethane under low mechanical agitation (100 rpm). The resin beads were placed at 0–5 °C under nitrogen atmosphere. 2.8 mL (29.1 mmol) of BBr_3 were added. After 7 h, the reaction mixture was poured slowly into ultra pure iced water. The resin beads were collected by filtration and extracted in a Soxhlet 24 h with water and 24 h with ethanol and then dried under vacuum for 3 days at room temperature.

2.4. Instrumentation and resin characterization

The chemical composition of resins was confirmed by FTIR spectroscopy (Nicolet, Nexus), and elemental analysis (CNRS Laboratory, Vernaison). FTIR spectroscopy was performed in transmission mode on KBr pellets (32 scans, resolution 4 cm^{-1}).

Nitrogen adsorption–desorption isotherms at 77 K were determined with a Micrometrics ASAP 2010 apparatus. Before the adsorption experiment the samples were evacuated several hours at a pressure lower than 10^{-3} Pa and a temperature of 50 °C.

Hydroxyl functions of DVB–DOH resins were determined by back titration (pH meter Methrom 702). Fifty milligrams of resin beads were put in a NaOH solution (5×10^{-3} mol L^{-1}, 50 mL) during 72 h under orbital agitation. Excess NaOH was titrated by a hydrochloric acid solution (2×10^{-3} mol L^{-1}). In the case of back titration with previous swelling by methanol, resins were first swelled with 200 μL of ethanol before the contact with the NaOH solution.

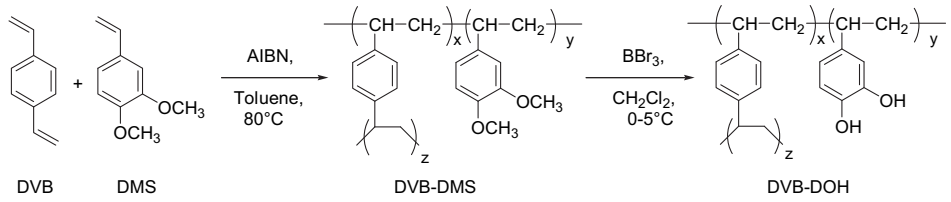
Water uptake ratios of resins were determined by thermogravimetrical analysis (TGA Q600, TA Instrument). The beads were put in water during 72 h (ambient temperature and orbital agitation), dried under atmospheric conditions during 24 h and then analyzed by TGA (isotherm at 110 °C during 1 h).

The densities of the resins were determined by pycnometry with ethanol.

The quantities of metal ions retained by gram of resins were determined as follow: 50 mg of resins were put in contact with 100 mL of a metal ion solution (5 mg L^{-1}) at pH = 8 for cadmium and pH = 6.5 for copper during 14 h. The remaining metal concentrations in the solution were measured by ICP–AES (ICP

Table 1
Copolymers preparation conditions; quantity of pendant vinyl groups (Q_{PV}) determined by IR; surface area determined by BET (S_{BET}), porous volume and average pore diameter determined by adsorption/desorption of nitrogen and density determined by pycnometry.

Copolymer		DVB(90)–DMS(10)	DVB(90)–DOH(10)	DVB(70)–DMS(30)	DVB(70)–DOH(30)	DVB(50)–DMS(50)	DVB(50)–DOH(50)	DVB(90)–St(10)
Dilution degree (%,v/v)	Toluene	50	_	50	_	50	_	50
	DVB	45	_	35	_	25	_	45
	DMS	5	_	15	_	25	_	0
	Styrene	0	_	0	_	0	_	5
Q_{PV} (mmol/g)		0.71	0.06	0.11	0.01	0.05	0.00	0.89
S_{BET} (m^2 g^{-1})		596	658	379	464	0	0	490
Porous volume (cm^3 g^{-1})		0.57	0.62	0.32	0.38	Non-mesoporous materials		0.38
Average pore diameter (nm)		3.8	3.8	3.4	3.3	Non-mesoporous materials		3.1
Density (g cm^{-3})		1.12	1.13	1.06	1.15	1.09	1.22	_



Scheme 1. Preparation of DVB-DMS and DVB-DOH copolymers

Vista MPX Axial EL 02024632, SPS 5 FL 02014805, AA 800S/N 94121123) with following parameters: power 1.2 kW, pump speed 15 mL min^{-1}, plasma flow rate 13.5 L min^{-1}.

The diffuse reflectance spectra of the resins were measured with a Perkin–Elmer 860 spectrophotometer equipped with a 15 cm diameter integrating sphere bearing the holder in the bottom horizontal position. They were recorded at room temperature in steps of 1 nm, in the range 200–800 nm with a bandwidth of 2 nm and the instrument was calibrated with a certified Spectralon white standard (Labsphere, North Sutton, USA). The Kubelka–Munk model [19] describes the light penetration in porous media using only two parameters (both with units of cm^{-1}), namely an absorption coefficient, k, and an isotropic scattering coefficient, s. This leads to a very simple relationship between infinite reflectance and absorption and scattering coefficient, known as the remission function, viz.: $F(R_\infty) = (1 - R_\infty)^2/2R_\infty = k/s$.

3. Results and discussion

3.1. Resin syntheses and characterization

Poly(vinylcatechol-*co*-divinylbenzene) resin beads were prepared according to Scheme 1. In a first step, 3,4-dimethoxystyrene (DMS) was copolymerized in suspension with divinylbenzene (DVB) using toluene as an inert diluent. The toluene is used to generate porous materials with a large surface area since toluene has a good thermodynamic compatibility with the polymer network and will cause late phase separation of solvent porogen during the copolymerization [7]. In addition, the ratio of DMS versus DVB was increased to study the effect of catechol content on the material properties (Table 1). In a second step, catechol functions were deprotected using boron tribromide.

In order to make easier the characterization of these resins by infrared (IR) spectroscopy, a reference resin (called DVB(90)–St(10)) was prepared replacing DMS monomer by styrene (Table 1).

Table 2
Evaluation of the quantity of catechol incorporated (mmol g^{-1}) by elemental analysis and acido-basic back titration, and water uptake ratio determined by TGA.

DVB(x)–DMS(100 − x) or DVB(x)–DOH(100 − x)		x		
		90	70	50
Molar fraction of DMS in DVB–DMS copolymer (%)	Theoretical	10	29	49
	Elemental analysis	11	32	46
Quantity of catechol in DVB–DOH copolymer (mmol g^{-1})	Elemental analysis[a]	0.82	2.07	3.16
	Back titration	0.09	0.37	0.60
	Back titration with prior contact with ethanol	0.27	0.40	0.61
Accessibility (%)		11	18	19
Water uptake ratio of DBV(x)–DOH(100 − x) (%)		1.5	2.8	4.9

[a] These values were calculated from elemental analysis of DVB–DMS resins assuming total deprotection of methoxy groups.

Characteristic ether bands were observed for DVB–DMS copolymers. Thus, the C–O stretching bands of aralkyl ether groups at 1238 and 1261 cm^{-1} are seen on the DVB(70)–DMS(30) spectrum (Fig. 1(b)). The C–H stretching band of O–CH_3 function at 2835 cm^{-1} appears close to the C–H stretching band of the polymer backbone (band of 2854 cm^{-1} observed on DVB(90)–St(10) spectrum). All those bands are missing from the DVB(90)–St(10) spectrum (Fig. 1(a)). Deprotection of the methoxy groups was assessed by the disappearance of bands at 2835 and 1238 cm^{-1} and the appearance of the broad O–H stretching band around 3416 cm^{-1} and C–O stretching and O–H deformation bands at 1279 and 1369 cm^{-1} (Fig. 1(c)).

Furthermore, IR spectroscopy was also used to estimate the quantity of pendant vinyl remaining groups according to the method of Bartholin et al. [20] (Table 1). As expected, the fraction of pendant vinyl groups decreases with decreasing DVB concentration. The deprotection of methoxy groups also generates a drastic decrease in the fraction of pendant vinyl groups. This is due to a post-crosslinking reaction catalysed by boron tribromide that mediates the Friedel-Craft's reaction of the vinyl groups with adjacent benzene rings.

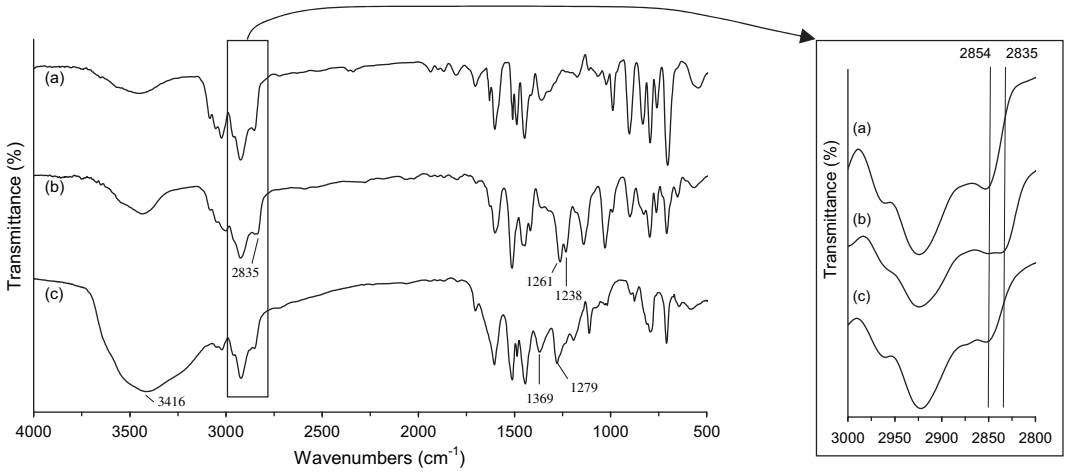


Fig. 1. FTIR spectra of copolymers DVB(90)–St(10) (a), DVB(70)–DMS(30) (b) and DVB(70)–DOH(30) (c).

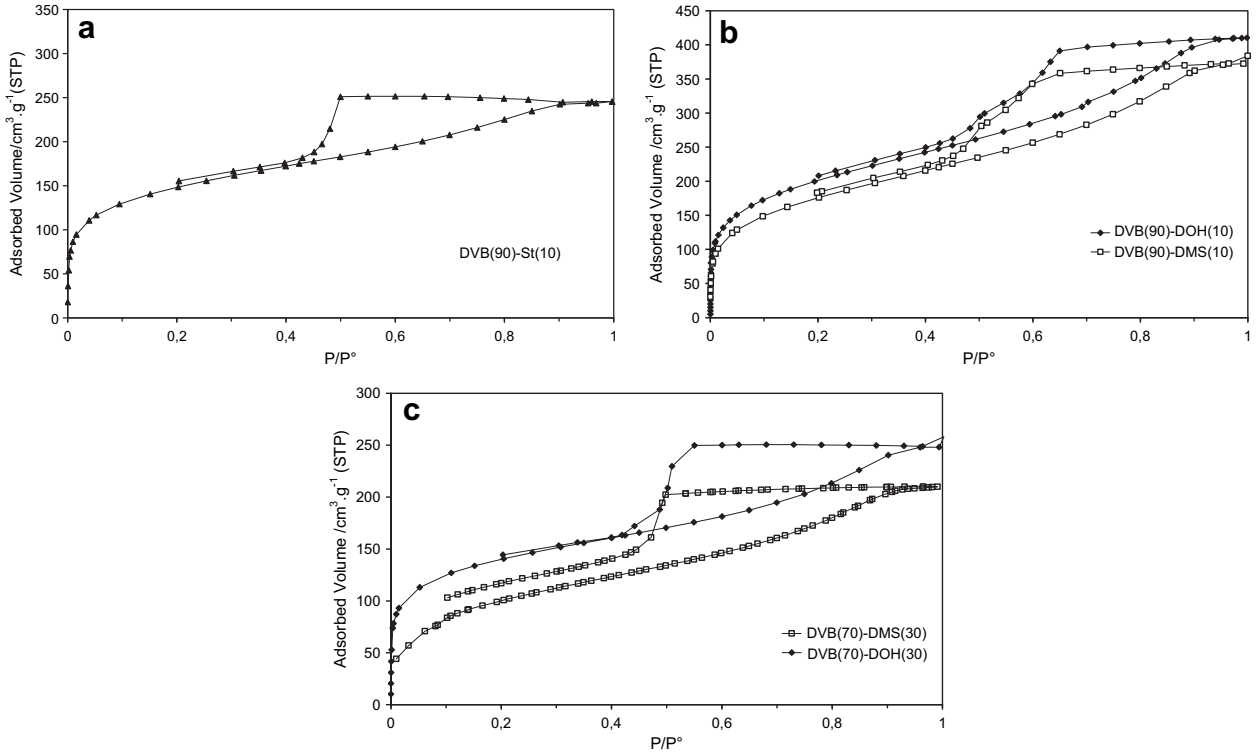


Fig. 2. Nitrogen adsorption/desorption isotherms of DVB(90)–St(10) (a), DVB(90)–DMS(10) and DVB(90)–DOH(10) (b), DVB(70)–DMS(30) and DVB(70)–DMS(30) (c).

Elemental analysis was used to evaluate the amount of DMS incorporated in the DVB–DMS copolymers. The molar fraction of DMS could be calculated from the %C/%O ratios (Table 2). Nevertheless, a quantitative determination of catechol in DVB–DOH copolymers was not possible most likely because of the higher hydrophilicity of these materials resulting in an overestimation of the oxygen content. The comparison of the molar fraction estimated by elemental analysis with the one calculated from the introduced proportions of DVB and DMS indicated that all the DMS did react with DVB and hence was incorporated quantitatively in the copolymers. It also made it possible to calculate a maximum catechol quantity (mmoles/per gram of resin) in the copolymers (assuming total deprotection of the methoxy functions). This was found to vary from 0.82 to 3.16 mmol g^{-1}.

The evaluation of the amount of catechol in the DVB–DOH copolymers was also carried out by titration of the hydroxyl groups. Direct titration was not possible since the equilibration period between each base addition was too long. For this reason, a back titration was done by first equilibrating the copolymers with an excess of sodium hydroxide solution followed by titrating this solution by a solution of HCl. Using the two pK_a values of catechol (9.46 and 12.70 [21]), the titration of catechol was simulated using similar conditions as for the case of the copolymers back titration. Since the pK_{a2} value of catechol is high, NaOH in excess deprotonates catechol at 95% in 2-hydroxyphenolate ($C_6H_4OHO^-$) and the remaining 5% are in the dibasic form ($C_6H_4O^-O^-$). Assuming that the copolymerization does not significantly modify the pK_a values of catechol, the amount of catechol per gram of resin was found to vary from 0.09 to 0.60 mmol g^{-1}. These values are significantly lower than those estimated by elemental analysis. For the copolymer DVB(90)–DOH(10), beads float on water surface in agreement with the very small water uptake ratio measured by TGA (Table 2). For this reason, a different procedure was implemented. It consisted in first swelling the resin with a small amount of ethanol before putting it

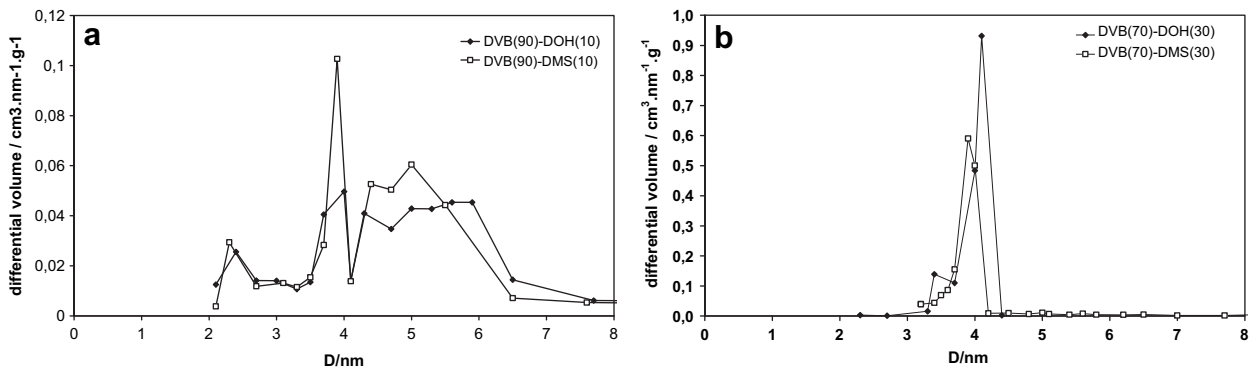


Fig. 3. Pore size distributions derived from the BJH method [24] applied to the desorption isotherm of DVB(90)–DMS(10) and DVB(90)–DOH(10) (a), DVB(70)–DMS(30) and DVB(70)–DOH(30)(b).

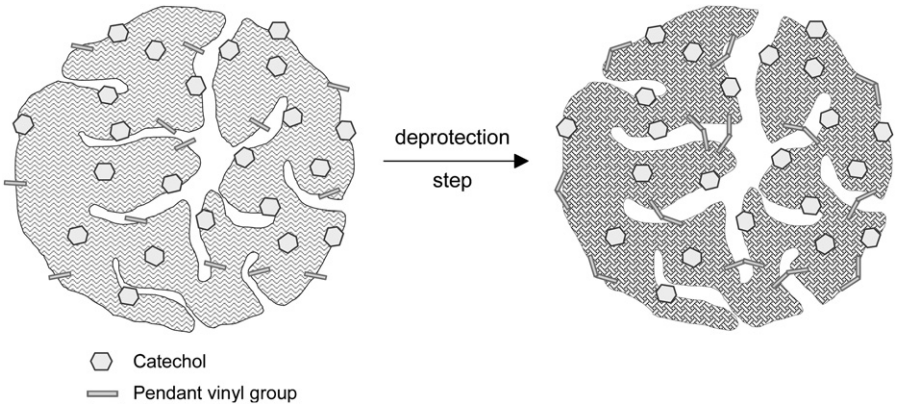


Fig. 4. Schematic representation of porosity before and after deprotection.

in contact with the basic aqueous solution. The gain of accessibility to hydroxyl groups is indeed quite significant for DVB(90)–DOH(10) but not for the other copolymers. It can be explained by the effective wetting of the polymer network in this case.

From elemental analysis and back titration, the accessibility (expressed in percentage) was calculated as being the ratio between the quantity of catechol measured by back titration (without prior contact with ethanol) and the maximum quantity of catechol determined by elemental analysis. As expected from its lower hydrophilicity, DVB(90)–DOH(10) gives the lowest rate. However in all cases, the accessibility rate was rather limited suggesting that although the incorporation of DMS was effective, the accessibility to hydroxyl functions of catechol is difficult. An explanation might be that the catechol units are embedded inside the polymer network. This could arise from the copolymerization process or be due to the post-crosslinking reaction which could restrict the access to catechol.

3.2. Resin pore structure

Nitrogen adsorption measurements were performed on the resins before and after deprotection. The adsorption–desorption isotherms are of type IV [6] (Fig. 2) indicating that those solids are mainly mesoporous according to the IUPAC nomenclature. The surface areas were determined from nitrogen sorption isotherms by using the Brunauer, Emmet and Teller (BET) treatment [22] and are given in Table 1.

Since adsorption and desorption curves are not parallel, it is likely that the mesopores are interconnected or have irregular shapes. The return of the adsorption branch on the adsorption is not perfect as often observed with organic adsorbents because of the diffusion of nitrogen between polymer chains.

Depending on the sample, the desorption branch presents one or two steps. The extension of the adsorption branches on a large pressure range indicates that mesopore size distributions are large (3–20 nm). On the other hand, the steps of desorption branches show the presence of constrictions or small pore entrances. A sharp fall in the relative pressure range 0.42–0.48 is observed, it corresponds to the return of the desorption branch on the adsorption branch. It may indicate that some pores may be connected to the outside by small entrances (smaller than 4 nm) that lead to a desorption mechanism by cavitation [23]. For DVB(90)–DMS(10) and DVB(90)–DOH(10), these constrictions are in two pore ranges: one around 5 nm and the second one below 4 nm (Fig. 2(b)). For DVB(70)–DMS(30) and DVB(70)–DOH(30), they are below 4 nm (Fig. 2(c)). It is worth noticing that all samples present a micropore volume (detected by the *t*-plot method) around 0.12 mL g^{-1}. Except for copolymers DVB(50)–DMS(50) and DVB(50)–DOH(50) which appeared to be non-porous, all samples give similar average pore diameters ranging between 3.3 and 3.8 nm, calculated as $D = 4V_p/S_{BET}$ where V_p is the total porous volume deduced from the amount adsorbed at saturation and S_{BET} is the surface area determined by BET. These values are not strongly affected by the DMS content, or by the deprotection step and they are smaller than those observed on the mesopore size distribution, derived from the Barett Joyner Halenda (BJH) method [24] (Fig. 3(a) and (b)), because of the presence of micropores.

Decreasing the molar fraction of DVB gives a decrease of both the pore volume and the surface area. This could be due to a lower degree of crosslinking that generates non-porous gel structures in the dry state. A complementary rationale may be found in the formation of the porous structures during crosslinking. The diluent used during the polymerization process influences the final porosity of the polymer material. If the diluent has a good affinity for the monomers and the copolymer, the phase separation will be late resulting in materials with a large surface area [8]. This is the case for toluene with styrene and divinylbenzene in the proportions of the DVB(90)–St(10) copolymer. Nevertheless, for the different DVB–DMS copolymers, the compatibility between toluene and the monomers and copolymer will vary and can be predicted by the solubility parameters (δ_i), using Hildebrand theory. Thus, the solvating power of the diluent is favoured when $\Delta\delta^2 = (\delta_1 - \delta_2)^2$ is minimized [25]. Increasing the concentration of DMS will have an impact on this thermodynamic compatibility since the solubility parameter of DMS ($\delta_{DMS} = 5.1$ (cal $cm^{-3})^{1/2}$) is rather far from those of DVB ($\delta_{DVB} = 8.9$ (cal $cm^{-3})^{1/2}$) and toluene

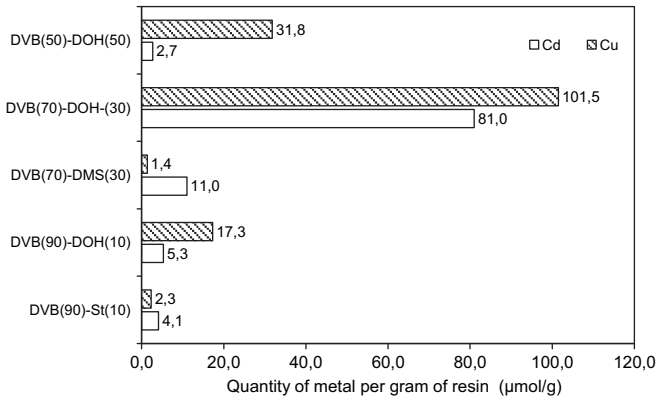


Fig. 5. Quantity of metal retained per gram of resin (µmol g^{-1}).

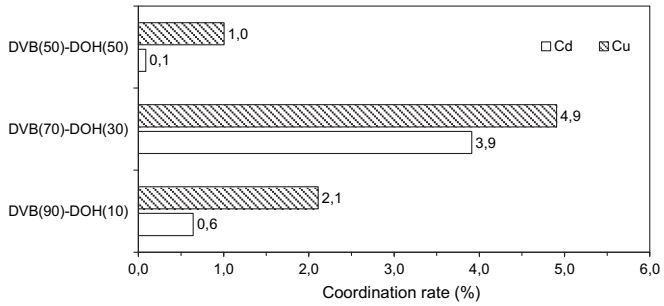


Fig. 6. Coordination rate calculated as the ratio of the quantity of metal retained by the quantity of catechol determined by elemental analysis.

($\delta_{Toluene} = 8.6\ (cal\ cm^{-3})^{1/2}$). The values of δ have been calculated for mixture of DVB and DMS in the proportions used for copolymers synthesis [26]: $\delta_{DVB(90)-DMS(10)} = 8.3\ (cal\ cm^{-3})^{1/2}$, $\delta_{DVB(70)-DMS(30)} = 7.8\ (cal\ cm^{-3})^{1/2}$ and $\delta_{DVB(50)-DMS(50)} = 7.2\ (cal\ cm^{-3})^{1/2}$. This leads to $\Delta\delta^2$ values from 0.08 for the mixture of monomers and toluene in DVB(90)–DMS(10) to 0.70 for DVB(70)–DMS(30) and 1.95 for DVB(50)–DMS(50). This last value is close from that of a poor solvating pore-forming agent ($\Delta\delta^2 = 2.40$ for DVB(90)–St(10) and *n*-heptane for instance). Poorly solvating diluents are known to lead to smaller surface areas [8].

Considering the cleavage of the methoxy groups, it causes a significant increase of the surface area for DVB(90)–DMS(10) and DVB(70)–DMS(30). In Fig. 3, mesopore size distributions show also a small shift of around 0.5–1 nm toward higher values. As shown by Davankov et al. [27], this is the result of the Friedel-Craft's alkylation reaction shown by IR (see above). According to Aleksieva et al. [28], the post-crosslinking reaction results in greater stability of the already existing pores by shrinkage of the walls rather than in the creation of new pores. This shrinkage is confirmed by the increase of density of the materials after deprotection (Table 1).

From this study of the resins pore structure, another hypothesis can be made to explain the small accessibility of the hydroxide ions to the hydroxyl function of catechol units. The adsorption/desorption of nitrogen indeed evidences that the connectivity between pores is restricted by their small entrances. This might also be a limiting factor for the access to catechol functions inside pores. Fig. 4 illustrates both hypothesis: (a) part of the catechol units are embedded inside the polymer network either during the copolymerization process or during the post-crosslinking reaction; (b) the presence of constrictions at the entrance of the pores limits their accessibility.

3.3. Complexing properties of the synthesized resins

Catechol is known for its chelating properties toward some metal ions. In particular, catechol can complex cadmium (II) and copper (II) with relatively high complexation constants ($\log K = 10.8$ and 14.1 respectively [29]). Quantities of those metals retained per gram of resin are shown in Fig. 5. As expected from complexation constants, copper is better retained by the poly(vinylcatechol-*co*-divinylbenzene) resins than cadmium. Best results are obtained for the DVB(70)–DOH(30) copolymer. This one is in between DVB(90)–DOH(10) and DVB(50)–DOH(50) in terms of quantity of incorporated catechol but in contrast to DVB(50)–DOH(50), it is a porous material with a large surface area. Weak coordination obtained for DVB(90)–DOH(10) can have two origins: the lowest quantity of catechol units and/or the small wetting capacity of the resin.

For a better comparison, retention of the metal ions was also performed on the DVB(90)–St(10) and DVB(70)–DMS(30) resins. The surface area of DVB(90)–St(10) resin is close to that of DVB (70)–DOH(30) but on the one hand, it does not contain hydroxyl groups and on the other hand, it has pendant vinyl groups. DVB (70)–DOH(30) appears significantly more efficient for retention of Cd(II) and Cu(II) than DVB(90)–St(10). Since both materials have comparable porosity, this confirms the importance of the hydroxyl groups of catechol for the retention of these metal ions. The observed affinity of DVB(90)–St(10) for cadmium and copper might be explained by the affinity of those metals with either the benzene ring or/and the vinyl pendant groups. As far as the deprotection step is concerned, its importance can be evidenced by the comparison of DVB(70)–DMS(30) and DVB(70)–DOH(30) results. As expected, it proves that methoxy groups are less efficient than hydroxyl groups for metal complexation.

In a previous work, we incorporated catechol by grafting on a commercial poly(styrene-*co*-divinylbenzene) resin [30]. For the best material (DVB(70)–DOH(30)), the metal retention was improved compared to grafting of catechol where we found capacities of 25.8 $\mu mol\ g^{-1}$ for Cd(II) and 89.7 $\mu mol\ g^{-1}$ for Cu(II).

A coordination rate (expressed in percentage) was calculated as the ratio of the quantity of metal retained by the quantity of catechol determined by elemental analysis (Fig. 6). The decrease of the coordination rate between DVB(70)–DOH(30) and DVB(50)–DOH (50) might be explained by the loss of porosity of the copolymer structure. Nevertheless, these low values of the coordination rate for copper and cadmium prove that catechol units are even less accessible to copper (II) and cadmium (II) ions than they were to hydroxide ions. As copper and cadmium hydrated ions are larger than hydroxide ions [31], the low accessibility might be assigned to reduced entrances of the pores.

It is very easy to visualise the retention of cadmium and copper by a simple observation of the coloration change upon complexation (Fig. 7). For this reason, those samples were studied by UV diffuse refletance spectroscopy (Fig. 8). In solution, catechol is characterized by an absorption band at 275 nm in its diprotonated form (C_6H_4OHOH) and a band at 289 nm in its monoprotonated form ($C_6H_4OHO^-$) [32]. The observation of one single absorption band at 280 nm on the DVB(90)–DOH(10) diffuse reflectance

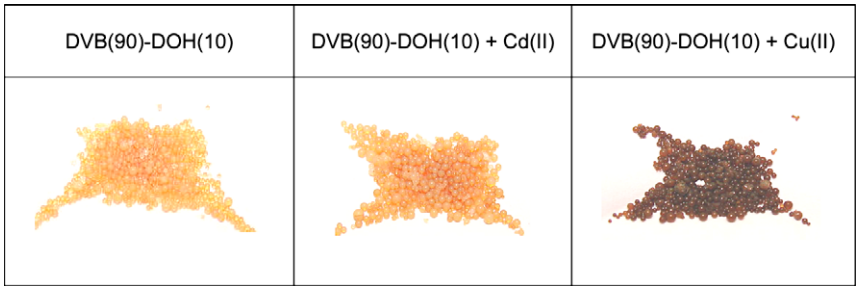


Fig. 7. Colour variation of copolymer DVB(90)–DOH(10) after contact with a Cd(II) or Cu(II) aqueous solution ($C = 5\ mg\ L^{-1}$).

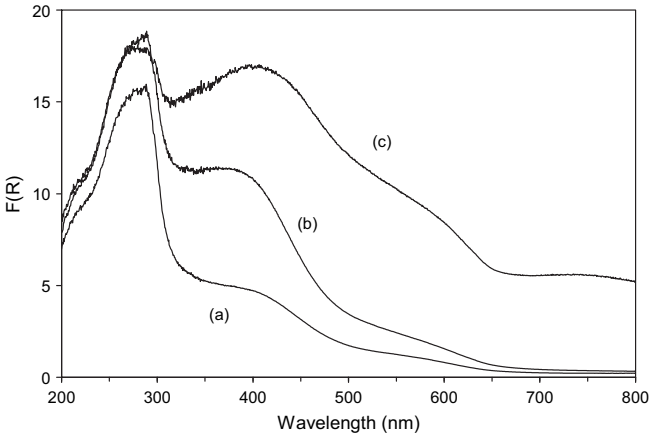


Fig. 8. UV–Visible diffuse reflectance spectra of DVB(90)–DOH(10) (a), DVB(90)–DOH (10) + Cd(II) (b) and DVB(90)–DOH(10) + Cu(II) (c) (same conditions as Fig. 5).

spectrum (Fig. 8(a)) proves that catechol is in its neutral form in accordance with its p*K*a values (9.46 and 12.70). The diffuse reflectance spectra significantly evolve upon complexation with cadmium and copper (Fig. 8(b) and (c)). Catechol can form in solution either brown-yellow Cu^{2+} mono-catecholate complex with absorption bands at 449 nm and 743 nm or medium-green Cu^{2+} bis-catecholate complex with absorption bands at 401 nm and 655 nm [33]. The presence of three bands at 400 nm, 570 nm and 750 nm on the diffuse reflectance spectrum of DVB(90)–DOH (10) + Cu(II) suggests that both mono and bis copper–catecholate complexes are formed with DVB(90)–DOH(10). This indicates that two grafted catechol molecules are sufficiently closed to enable such a complexation. The binding of the cadmium in solution does not induce significant variations in the absorption spectra. For the copolymer DVB(90)–DOH(10), it is evidenced by the apparition of a band at 370 nm suggesting probably the presence of a mono-catecholate complex. These variations of coloration of DVB–DOH resins put in contact with metallic ions seems very interesting as a potential method to determine the presence of theses species.

4. Conclusions

In the present paper, we introduced catechol in a macroporous resin by copolymerization of a monomer derived from catechol while we did previously incorporate it by chemical modification of a commercial poly(styrene-*co*-divinylbenzene) resin [30]. The functional monomer, 3,4-dimethoxystyrene, needed to be deprotected to recover the hydroxyl functions of catechol. During this deprotection step, post-crosslinking was induced by the use of boron tribromide. As a result of the use of toluene as a porogen and the post-crosslinking reaction, we obtained poly(vinylcatechol-*co*-divinylbenzene) resins with large accessible surface area. From elemental analysis, we proved that dimethoxystyrene monomer was totally incorporated in DVB–DMS copolymers.

Accessibility to catechol units was evaluate in static mode and appeared to be low. As expected, it was also dependent of the size of the considered species since it decreased from hydroxide to metallic ions. However, the metal retention was improved compared to grafting of catechol.

This low accessibility can be the result of the morphology of the resin beads and of the bottle-shape form of the pores (restricted connectivity between the pores). Moreover, catechol units might be embedded inside inaccessible cores of highly crosslinked nodules as a result of the copolymerization process or of the post-crosslinking during methoxy deprotection step. Nevertheless, significant coloration variations were observed in presence of Cd(II) and Cu(II) ions opening further prospects in terms of metal identification and/or quantification.

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