Macroporous Polyamines Containing Cyclodextrin: Synthesis, Characterization, and Sorption Properties

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ABSTRACT: Macroporous beads containing *N*-vinyl-tertio-butyl carbamate (NVTBC) have been prepared by suspension copolymerization using divinylbenzene as crosslinking agent. After solvolysis, parent copolymers containing vinylamine (VA) were functionalized by β-cyclodextrin (β-CD) using the mono-tosyl derivative of β-CD as the intermediate (β-CDOTs). Several copolymers with various degrees of substitution were synthesized. Several factors (reaction time, amounts of the reactants, composition of solvent, and temperature) were studied. Characterization was achieved by crosspolarization magic angle spinning nuclear magnetic resonance spectroscopy (CPMAS NMR). The textural features (specific area and porous volume) of the beads were also determined. These insoluble macroporous copolymers containing β-CD were then used for the recovery of various organic pollutants from aqueous solutions. Some preliminary studies (time, concentration, kinetics, and β-CD content) are presented here. The results of sorption experiments show that they exhibit high sorption capacities toward substituted benzene derivatives. The mechanism of sorption is an acid-base interaction due to the amino groups of the polymer network and/or the formation of an inclusion complex due to the β-CD molecules. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1419–1427, 1998

Key words: macroporous polyamines; cyclodextrin; sorption properties; characterization

INTRODUCTION

In previous works,[1–5] we prepared new organic sorbents based on macroporous poly(vinylamine) with high specific areas and containing primary amino groups. It was found that these sorbents

exhibit high sorption capacities toward metal ions such as uranium[4] or copper.[5] In this work, we have exploited the property of β-cyclodextrin (cyclomaltoheptaose or β-CD) to form inclusion complexes with various molecules. β-CD is a torus-shaped cyclic oligosaccharide, made up of seven α-1,4–linked D-glucopyranose units (Scheme 1) with a hydrophobic cavity. It is well known that this structure gives rise to a remarkable ability to form inclusion complexes in solution or in solid state with organic molecules, especially phenolic derivatives, through host–guest interactions. The
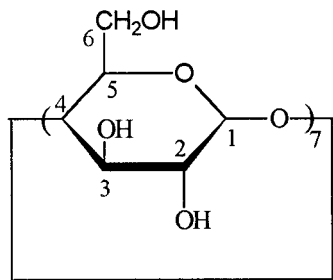
Scheme 1 Structure of beta-cyclodextrin (β-CD).

ability to form inclusion complexes depends on the size and polarity of the guest molecule and its shape,[6] hence, β-CD complexation is a procedure of choice for depollution techniques.

In this article we describe the synthesis and characterization of a series of vinylamine-based crosslinked copolymers containing β-CD. We have functionalized with β-CD the above macroporous polyamines using the mono-tosyl derivative of β-CD as intermediate (β-CDOTs). Solid-state ^{13}C-nuclear magnetic resonance (NMR) techniques such as crosspolarization magic angle spinning with dipolar decoupling (CPMAS) and magic-angle spinning (MAS) have been used to characterize and differentiate between sections of these materials with different molecular mobilities. The complexing properties of these insoluble poly-amines toward organic pollutants were determined by the batch method. The influence of several parameters (time, concentration, kinetics, and β-CD content) on the sorption capacity of these copolymers with respect to organic compounds is evaluated.

EXPERIMENTAL

Materials

N-Vinyl-tertio-butyl carbamate (NVTBC monomer), precursor of vinylamine, was the main component of the copolymers and was prepared according to Hart,[7] and Hughes and St Pierre.[8] Styrene (ST), the comonomer, was a commercial product (Janssen Chimica, Beerse, Belgium) used as received. The crosslinking agents were divinyl-benzene (DVB) and ethylene glycol dimethacrylate (DMG): these two products (Merck) were used without further purification. β-CD supplied by Janssen Chimica was recrystallized from water and dried overnight under vacuum at 100°C. Other compounds were purchased from various

suppliers and were used without further purification. The macroporous polyamines containing β-CD were prepared in three steps: (1) suspension copolymerization using divinylbenzene as cross-linking agent, (2) solvolysis of the protecting amino groups, and (3) functionalization of these amino groups by β-CD using the mono-tosyl derivative of β-CD as the intermediate (see Scheme 2).

Copolymerization

We applied the technology introduced by Tbal et al.[1-4] with some modifications to increase the quantity of vinylamine present in the copolymer and the degree of crosslinking to the minimum required for mechanically stable polymers. Resins were prepared by suspension copolymerization in the presence of heptane as a porogenic agent to obtain porous copolymers. A typical copolymerization was as follows (GD40 in Table I): The manipulation was carried out under N_2. Into a reactor, 3.8 g of accacia powder and 12 g of NVTBC are poured in 154 mL of water and heated at 80°C under stirring (220 rpm). Separately, the organic phase is prepared as follows: 6 g of DMG, 5 g of DVB, and 9 g of ST are dissolved in 19 mL of heptane. This mixture was added to the reactor after dissolution of the accacia powder and the melting of the NVTBC monomer. Azo-bis-isobu-tyronitrile (0.3 g) (AIBN used as initiator at a concentration of 1% of the monomer mixture) was
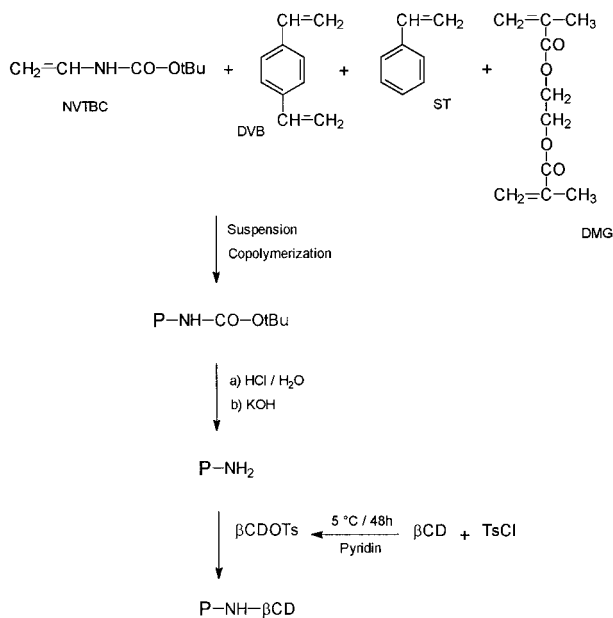
Scheme 2 Synthesis of macroporous copolymer containing beta-cyclodextrin.

then added. When the suspension was well established, 3.1 mL of an ammoniacal salt of a copolymer of styrene and maleic anhydride (dispersing agent) was added. After 1 h the sticking point occurs and the stirring speed was then increased to 450 rpm to avoid coalescence. Fifteen minutes later, the gel point is attained and the beads were no longer sticky. The stirring speed was then reduced to 220 rpm and the reaction mixture is stirred for 8 h. During this period, the beads harden and acquire their mechanical properties. The beads (series GDXX) were then decanted off and washed with water. The diluent (heptane) was extracted with methanol in a soxhlet for 24 h and the beads were dried for 24 h at 60°C under vacuum.

Solvolysis

The tertio-butyl carbamate protecting groups in the precopolymers were removed by HCl in ethanol. One gram of beads GDXX were mixed with 5 mL of ethanol with stirring and 20-fold excess of concentrated HCl was added at room temperature. This mixture was stirred for 24 h. The beads (in the NH^{3+}, Cl^- form) were then filtered off and washed with distilled water until neutral pH. Finally, the beads (series GDXXS) were extracted with methanol in a soxhlet for 24 h and dried under vacuum at 60°C for 24 h.

Functionalization

The synthesis of β-CDOTs was the same as described in a previous work.[9] The beads were previously treated with an excess of KOH 1M to obtain free amino groups (residual chloride <1%). A typical grafting reaction was carried out as follows (GD65242 in Table IV): 3 g of β-CDOTs were dissolved in 45 mL of a methanol : dimethylacetamide (2/1 V/V) mixture. One gram of resin GDXXS was added to this suspension and the mixture was kept at 50°C for 24 h. After cooling, the beads (series GDXX with CD) were filtered, washed, with methanol and acetone, then dried under vacuum at 60°C for 4 h.

Methods

The amount of vinylamine per gram of bead in the precopolymers containing the NVTBC residue and in the copolymers resulting from solvolysis were obtained from the results of elemental analysis of nitrogen and chlorine. The method used for the determination of the amount of β-CD immobi-

lized onto the beads was the determination of reducing sugars with tetrazolium blue after acidic hydrolysis, as described earlier.[10] The surface area (Ssp in m^2/g) was obtained from nitrogen adsorption−desorption measurements following the BET method (apparatus Quantasorb Jr). Mercury porosimetry (apparatus Carlo Erba 800) was used to determine the porous volume (V_p in cm^3/g) and the average pore radius (r in Å). Solid-state ^{13}C-NMR techniques, crosspolarization (CP), and magic angle spinning (MAS) were used for the characterization of the different supports. The spectra were recorded with a Bruker CXP-300 spectrometer operating at 75.47 MHz. The following conditions were applied: repetition time 5 s, ^{1}H 90° pulse length 4.6 μs, contact time 1 ms, acquisition time 30 ms, spin rate 4000−4200 Hz, and 303°K. The compounds were placed in a Zirconium rotor, 7 mm in diameter and 21 mm high. The chemical shifts were referenced to tetramethylsilane via benzene as a secondary reference. The sorption capacities of the insoluble beads were determined in pure water or buffered solutions (pH 6 or 11) using the batch method. The resin (20 mg) was added to 5 mL of an aqueous solution of aromatic compound at known concentration in a tightly closed flask that was shaken at room temperature. The residual concentration of the organic solute was determined by spectrophotometry and the sorption capacity calculated. All solutions were filtered before measurements (0.2-μm Millipore filters).

RESULTS AND DISCUSSION

Copolymerization

To obtain organic resins with a different amount of β-CD and maximum accessibility of the β-CD cavity, we have prepared by suspension copolymerization using AIBN as initiator and using

Table I   Composition of Different Monomer Mixtures

Sample	NVTBC[a]	ST[a]	DMG/DVB[a]	HEPTANE[b]
GD40	40	30	20/10	30
GD60	60	10	20/10	30
GD65	65	5	20/10	30

[a] Expressed as percent by weight of the total monomer content.
[b] Expressed as percent by weight of the total organic phase.

Table II   Chemical and Physical Features of the Beads GDXX

Sample	NVTBC[a]	NVTBC (mEq/g)	DMG[a]	DVB/ST[a]	D[b] (μm)	Ssp (m²/g)	V_p (cm³/g)	r (Å)
GD40	25	1.75	22.5	52.5	31	41	0.4	195
GD60	50	3.5	19	31	31	68	0.7	206
GD65	58	4.05	18	24	21	80	0.9	226

[a] Expressed as percent by weight of the total in the resin content.
[b] D for average diameter in μm.

DMG and DVB as a crosslinking agent, three kinds of of macroporous beads (GD40, GD60, and GD65) (Table I). It was found that to obtain a high specific area it was necessary to use at least 30% of heptane (porogenic agent).[1,3] The utilization of the DMG/DVB mixture represent a compromise between the quality of these two monomers. As a matter of fact, DVB gives copolymers poor in NVTBC but with elevated surface area, and DMG provides a good incorporation of NVTBC but gives resins with low surface area.

Poly(vinylamine) Content

The results show that using different amounts of NVTBC and styrene it is possible to obtain beads with different vinylamine content (Table II). The amount of NVTBC and DMG were obtained from the results of elemental analysis of nitrogen and oxygen, respectively. The physical features of the beads GDXX are also reported in Table II. The results show that when we increase the amount of NVTBC the values of Ssp, V_p, and r increase: this is due to the fact that the interactions between the heptane (porogenic agent) and the corresponding homopolymer of NVTBC (monomer) are low, and then the pore size increases.

Solvolysis Step

The results of the yield of solvolysis show that the extent of the conversion of the tertio-butyl carba-

mate groups into vinylamine groups never exceeds about 75% (the highest value obtained was 76% for sample GD65) (Table III). The solvolysis is never complete: this is due to the fact that it is not easy to access all the protecting groups of the vinylamine units in the crosslinked network. The solvolysis step has no definite effect on the texture features of the three series of beads. The values of specific area obtained are the same. The GD65S polymer had a specific area of 80 m²/g, a porous volume of 0.9 cm³/g and contained 4.05 mEq/g of amino functions. It was then (as series GD40S and GD60S) subjected to a series of functionalizations by β-CD to introduce a complexing agent.

β-CD Content

After solvolysis, parent polymers containing vinylamine were functionalized by β-CD using the mono-tosyl derivative of β-CD as the intermediate. Table IV gives the reaction conditions: temperature, reaction time, composition of solvent, and amount of β-CDOTs. For a given GDXXS series, the degree of substitution is dependent on the ratio of VA/CDOTS. Best results are obtained with GD65S beads (due to the fact that these beads contain a more significant quantity of vinylamine), and also with increasing quantities of β-CDOTs and with increasing reaction times. Solvent has a less important influence.

Table III   Characteristics of the Beads after Solvolysis (Beads GDXXS)

Sample	VA, HCl[a]	R[b]	Ssp (m²/g)	V_p (cm³/g)
GD40S	1.45	74	40	0.4
GD60S	3.29	73	70	0.7
GD65S	4.16	76	85	0.9

[a] From elemental analysis for nitrogen and chlorine, in mEq/g.
[b] Yield of solvolysis in %.

Table IV   Synthesis and Characteristics of Resins Containing β-CD (Beads GDXXCD)

Sample	VA/CDOTs[a]	t in h	T in Ψ	Solvent	β-CD[b]	Ssp[c]
GD4021	0.5	48	50	MeOH/DMAC	21	61
GD4017	0.5	24	60	MeOH/DMAC	17	44
GD4010	1	24	60	MeOH/DMAC	10	39
GD6061	0.5	24	60	MeOH/DMAC	61	72
GD6032	1	24	60	MeOH/DMAC	32	
GD6029	1	24	60	MeOH	29	86
GD6011	1.7	25	70	H₂O	11	
GD6016	1.7	48	70	H₂O	16	52
GD6020	1.7	24	70	MeOH	20	
GD65319	0.5	12	50	MeOH/DMAC	319	89
GD65420	0.5	24	50	MeOH/DMAC	420	
GD6589	0.5	24	50	H₂O	89	62
GD65163	0.5	24	50	MeOH	163	65
GD65432	0.5	48	50	MeOH/DMAC	432	50
GD65242	1	24	50	MeOH/DMAC	242	53
GD65184	1.5	24	50	MeOH/DMAC	184	53
GD65169	2	24	50	MeOH/DMAC	169	
GD65177	2.7	24	50	MeOH/DMAC	177	
GD65109	4	24	50	MeOH/DMAC	109	95

[a] Molar ratio.
[b] From spectrophotometry method in μmol/g.
[c] Surface area in m²/g.

NMR Analysis

In Figure 1 the solid-state ¹³C CPMAS (left) and MAS (right) spectra are shown for three derivatives, GD60, GD60S, and GD40S. With the CPMAS technique it is possible to observe both the rigid and mobile components, while the MAS method principally shows signals arising from the mobile component. This can be seen in Figure 1(A) and 1(B)—the signal for the methyl carbons of the tertio-butyl group can clearly be seen in both CPMAS and MAS spectra at 29 ppm, while the other polymeric signals are much more easily seen in the former. In Figure 1(A) the phenyl carbons can be seen between 115 and 165 ppm, the carbonyl groups at about 180 ppm, aliphatic carbons from the main polymer chain between 15 and 85 ppm, and the methyl group arising from the terminals of the alkyl chains of DMG at 19 ppm. After the hydrolysis step the diminution of the signal of the tertio-butyl signal at 29 ppm is apparent from both GD60S and GD40S [Fig. 1(C) and 1(E)] confirming the deprotection of the amino function. In Figure 1(C), which corresponds to a compound containing higher levels of amine groups, the intensities of main chain carbon signals are apparent while in Figure 1(E), which corresponds to lower amine content, pro-

portionally lower intensities are observed for these signals compared to the phenyl signals. The CPMAS spectra shown in Figures 1(A), 1(C), and 1(E) can be considered comparable with each other but are not comparable with the MAS spectra shown alongside, Figures 1(B), 1(D), and 1(F). However, the MAS spectra are not directly comparable with each other because they were recorded under different conditions. Under similar conditions, the intensities of the signals in the three spectra are broadly similar, indicating comparable mobility of the material (results not shown). Verification of this is underway from relaxation measurements.

In Figure 2(A) and (B) the CPMAS and MAS spectra of GD65S sample are shown, respectively. The appearance of these spectra are very similar to those of GD60S, as shown in Figures 1(C) and 1(D). Figure 2(C) and 2(D) show the CPMAS and MAS spectra of the same material grafted with 163 μmol of β-CD per gram of copolymer GD65163. The signals corresponding to the glucose residues (C-1 to C-6) are clearly visible between 55 and 115 ppm. In the MAS spectrum [Fig. 2(D)], the intensities of the β-CD signals are relatively intense, indicating that this part of the material is relatively mobile. These two spectra confirm the presence of two components (polyamine
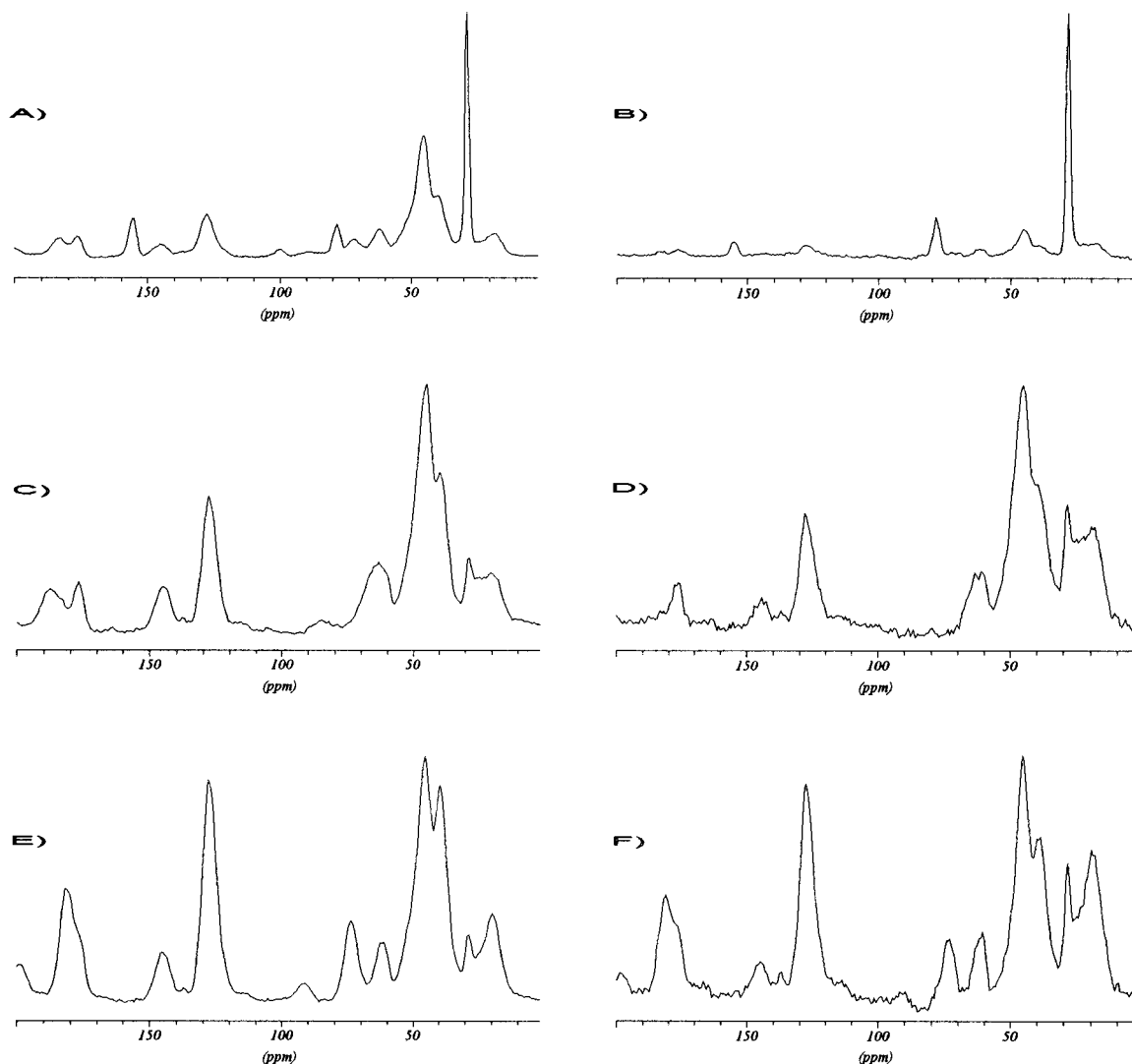
Figure 1 (A), (C) and (E) CPMAS spectra of GD60, GD60S, and GD40S polymers, respectively; (B), (D) and (F) MAS spectra of GD60, GD60S, and GD40S polymers, respectively.

network and β-CD molecules) in the materials. The molecular mobilities of these two components are being analyzed in terms of relaxation parameters such as ^{13}C spin lattice relaxation (T_1) and ^{1}H spin lattice relaxation in the rotating frame ($T_{1\rho}$).

Batch Experiments

Aromatic compounds, in particular chlorophenols, have been the subject of increasing interest recently as a result of increasingly stringent restrictions on the organic content of industrial effluents.[11-14] These compounds are the products of many industrial processes and occur in trace quantities in industrial waste water. It would, therefore, be advantageous to have adsorbant resins able that are to eliminate them. The sorption capacity of the polyamines was investigated using phenol (P), p-nitrophenol (pNP), benzoic acid (BA), β-napthol (BN), and chlorophenols (ClP) as model guest solutes. 4-Tertio-butyl-benzoic acid (TBBA) was also tested because this compound, according to the high value of the association constant ($K = 10^4 M^{-1}$) calculated by Wenz[15] with microcalorimetry, forms a very stable complex with β-CD in solution. K for the pNP compound is $1020 M^{-1}$. The capacities of these resins containing β-CD toward pollutants are compared with the original resins. Several parameters
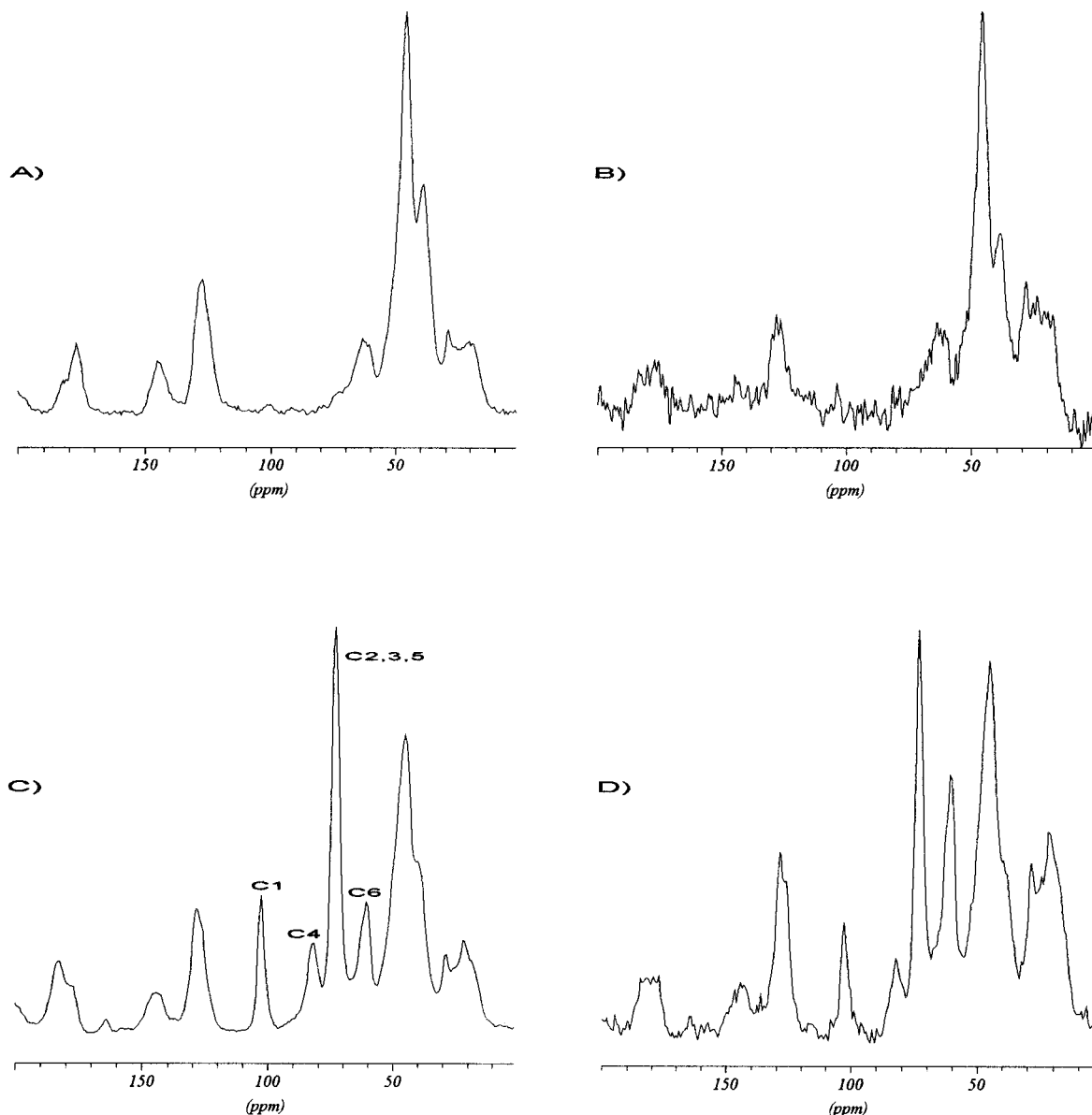
Figure 2 (A) and (B) CPMAS and MAS spectra of GD65S polymer respectively; (C) and (D) CPMAS and MAS spectra of GD65163 polymer, respectively.

(time, concentration, kinetics, and β-CD content) have been studied.

Figure 3 shows the sorption capacity of GD65S and GD65242 polymers versus stirring time toward pNP solute. The kinetics of sorption are very fast; the maximum capacity is obtained after 30 min. For the next experiments, 2 h are sufficient for reaching the plateau. The beads without β-CD exhibits high sorption capacities: this can be explained by the presence of acid–base interactions (ion exchange, hydrogen bonding) between the amino groups of the resin and the pNP solute (pK = 7.15). The average percentage uptake of GD65S beads is 40. When the resin contain β-CD molecules, we note an important increase of the sorption capacity (uptake 80%). If we express the results in function of the surface area of each resin (capacity in μmol/m^2) we note that the capacity is multiplied by a factor of 5 in presence of β-CD. We can assume that the formation of an inclusion complex due to the β-CD molecules and an acid–base interaction due to the amino groups of the polymer network are involved in the mechanism of sorption.

Figure 4 shows the sorption capacity of GD65S and GD65242 polymers versus starting concentration of pNP using a contact time of 2 h. The quantity
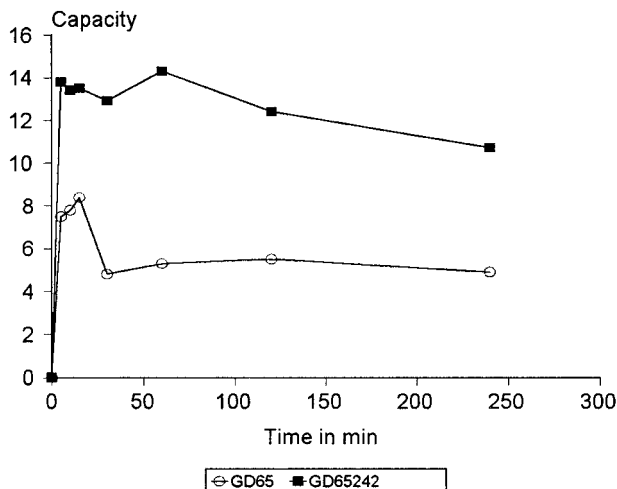
Figure 3 Kinetics of sorption capacity (in μmol/g) of pNP by GD65S and GD65242 Polymers in water (concentration 5 10^{-5} mol/L).

of polymer was kept constant while the molar concentration of the pNP guest molecule was varied between $5 \cdot 10^{-4}$ and $5 \cdot 10^{-3} M$. For concentrations superior to $5 \cdot 10^{-3} M$ we encountered some problems of solubility. The quantity of the retained pNP compound depends on the concentration of its aqueous solution and increases with an increase of the starting concentration. The quantity of pNP adsorbed by the resin without β-CD is shown by open circles corresponding to the quantity adsorbed due to acid–base interactions. The solid squares show the quantity adsorbed by the resin containing β-CD. The difference between the two is the quantity adsorbed by the β-CD molecules. It should be noted than this quantity is greater than the amount of βCD present in the resin. This excess can be explained by the presence of guest–guest (hydrophobic) interactions, which cause an accumulation of guests at the surface of the polyamine.

The results in Table V show that the order of the sorption capacity for the pollutants examined in pure water (pH $\sim$ 6) with a starting concentration of $5 \cdot 10^{-4} M$ is the following: β-napthol (BN) > p-nitrophenol (pNP) > benzoic acid (BA) > phenol (P). The sorption is much greater in the case of compounds that present compatible size, steric arrangement, and hydrophobicity with the β-CD cavity.[6] It is well known that β-napthol[16] and para-nitrophenol[17] form stable inclusion complexes with β-CD, while on the other hand, phenol[6] forms a less stable complex. The tests have also been carried out in buffer solutions at pH 6 and 11. We observe for pNP a significant decrease in the sorbed quantity at pH 11: this reflects the

fact that the inclusion complex with β-CD and aromatic derivatives are less stable at pH 11 than in pure water (pH $\sim$ 6).[9] For P, BN, and BA compounds the sorption capacity at pH 11 is near zero. Chlorophenols, insoluble molecules in water, exhibit high sorption at pH 11 using these polymers (Table V). We note that in these basic conditions, the order of their affinities is as follows: 2, 4, 6 ClP > pNP > 2, 4 ClP > pClP > mClP. These results can be explained by the different ionisation of the solute with the various pH used. In the pH 6 buffer, the results for these compounds are very similar to those obtained in pure water with nearly the same pH. The TBBA compound was found to be insufficiently soluble in water at the concentration of $5 \cdot 10^{-4} M$, and the comparison with the other compounds was carried out at $5 \cdot 10^{-5} M$. The order of the sorption capacity for the pollutants (BN, pNP, P, and TBBA) examined in water with a starting concentration of $5 \cdot 10^{-5} M$ and 2 h of stirring time is the following: BN (17 and 26.1 μmol/g) > pNP (14 and 20.7 μmol/g) > TBBA (6 and 15.7 μmol/g) > P (2 and 5 μmol/g); the first value is obtained using the GD60 polymer (without cyclodextrin) and the second using the GD6061 polymer (with cyclodextrin). The value of the sorption capacity of the TBBA is lower than expected even if the association constant between TBBA and the β-CD is very significant. This shows not only that the β-CD plays an important role in the sorption mechanism, but that there are also other interactions

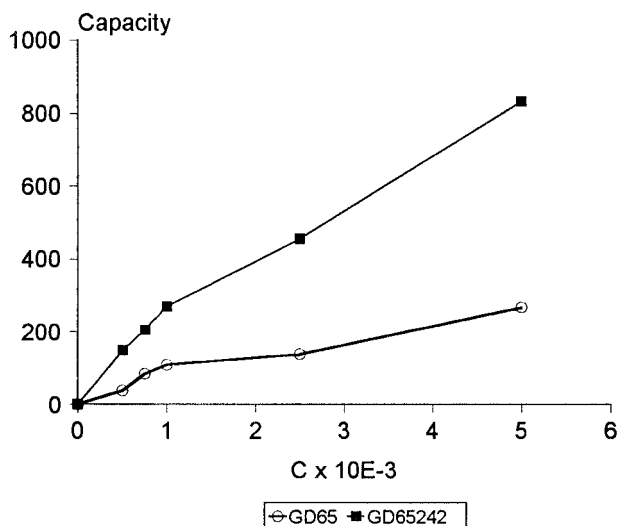**Figure 4** Capacity (in μmol/g) vs. starting concentration of pNP in water (polymers GD65S and GD65242; time 2 h).

Table V Sorption Capacity of Several Pollutants Using Several GD Polymers in Water and at pH

Sample	β-CD[a]	Capacity[a]								
		P[b]	pNP[b]	BN[b]	BA[b]	pNP[c]	pClP[c]	mClP[c]	2,4ClP[c]	2,4,6ClP[c]
GD40	0	54	113	136	126	76	73	66	76	147
GD4021	21	67	109	148	136	88	87	68	78	165
GD60	0	86	116	136	127	95	0	3	8	3
GD6016	16	57	126	143	136	105	73	76	76	163
GD6032	32	61	135	131	157	119	71	70	70	161
GD6061	61	27	124	148	136	102	82	65	85	172
GD65	0	3	79	83	41	63	33	22	28	54
GD65163	163	64	115	132	126	92	66	142	171	197
GD65242	242	79	143	113	105	102	100	103	129	154
GD65432	432	88	120	136	122	90	81	167	176	115

[a] In μmol/g.
[b] Distilled water.
[c] pH 11.
Time = 2 h; concentrations $5 \ 10^{-4}$ mol/L).

such as acid–base interactions (ion exchange, hydrogen bonding) due to the polyamine network and guest–guest hydrophobic interactions.

CONCLUSION

In this work, we have prepared macroporous copolymers containing vinylamine functionalized by beta-cyclodextrin. These insoluble materials have been characterized by solid-state ^{13}C-NMR techniques that allow the assignment of the principal ^{13}C signals to be made and confirm the various steps of the synthesis. These adsorbents possess specific inclusion recognition capabilities with aromatic compounds. The results of sorption experiments indicate that they exhibit high sorption capacities toward benzene derivatives (in particular, toward chlorophenols). The proposed sorption mechanism involves several kinds of interactions: acid–base interactions (ion exchange, hydrogen bonding) due to the polyamine network, interactions due to the formation of an inclusion complex with β-CD, and also guest–guest hydrophobic interactions. Our next objective will be to find the relationship between their retention behavior and molecular structure to analyze the molecular mobilities of the β-CD.

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