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Microwave-assisted immobilization of β-cyclodextrin on PEGylated Merrifield resins

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Abstract—β-Cyclodextrin was immobilized on PEGylated Merrifield resin through cross-linking with 1,6-hexamethylene diisocyanate (HMDI) reagent, using conventional and microwave-assisted methodologies. FT-IR analysis of the solid intermediates indicated the attachment of the linker arm to the resin due the appearance of characteristic bands centered at 1716 and 2270 cm^{-1} and the attachment of cyclodextrin to the resin was accompanied with increased absorption at the OH stretching regions (3330–3400 cm^{-1}). β-Cyclodextrin linked PEGylated resins are water insoluble and can be used to trap volatile organic compounds (VOCs) from water and subsequently be analyzed by headspace HS/GC, after simple filtration and drying steps.

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of six or more D-glucopyranose units connected through α-(1,4) glycosidic linkages. The apolar cavity in the center of the molecule is capable of forming host–guest type inclusion complexes with various organic molecules possessing suitable geometry and physical properties. They have been utilized extensively in chromatographic separations and purification methods.[1] The practical utility of cyclodextrins could be extended further if they can be rendered water insoluble. Different strategies have been explored in the literature including polymerization procedures[2–4] and immobilization onto solid particles such as silica,[5] chitosan,[6] and inside nanoporous oxides.[7] As part of our ongoing investigation on the applications of the PEGylated Merrifield resins,[8] we report here their use as resins to immobilize β-cyclodextrin using 1,6-hexamethylene diisocyante (HMDI) as a linker (see Fig. 1). In a typical experiment, PEGylated Merrifield resin[8] (1.00 g ± 0.05 g) was suspended in excess HMDI solution in toluene (10 mL, 10% (v/v)) with few drops of Tin(II) 2-ethylhexanoate. The mixture was stirred at room temperature for 2 h and the supernatant was removed by pipetting. The resin was washed several times with toluene and was dried under nitrogen. Excess β-cyclodextrin solution in DMF (10 mL of 10% (w/v)) and a few drops of Tin(II) 2-ethylhexanoate was then added to the resin. The mixture was stirred overnight and the supernatant was removed by pipetting. The product was filtered and washed with DMF, water, ethanol, and water again, and was dried under nitrogen.

The attachment of the linker arm HMDI onto the PEGylated Merrifield resin yielded 99.4% and a load of 0.598 mmol HMDI/g resin (see Table 1). The appearance of absorption bands centered at 2270 and 1716 cm^{-1} in the IR spectrum[9] (Fig. 2b) indicated the presence of isocyanate and urethane groups, respectively, confirming the attachment of the linker to the resin. The increased absorption bands at O–H stretching regions (3330–3400 cm^{-1}) in Figure 2c indicated the attachment of β-cyclodextrin moiety. However, the presence of the isocyante group (N=C=O) at 2270 cm^{-1} (see Fig. 2c) suggested that there are remaining reactive sites and that the reaction did not go to completion. The percentage yield obtained was 62.3%. To improve the yield of the second step, the immobilization of β-cyclodextrin on MRPEG–HMDI was also carried out under microwave irradiation at atmospheric pressure, the microwave was operated under constant temperature mode such that the power was varied to maintain a value of 70 °C for a total of 30 min using the Synthewave™ 402 (Prolabo, France). The FT-IR analysis has indicated

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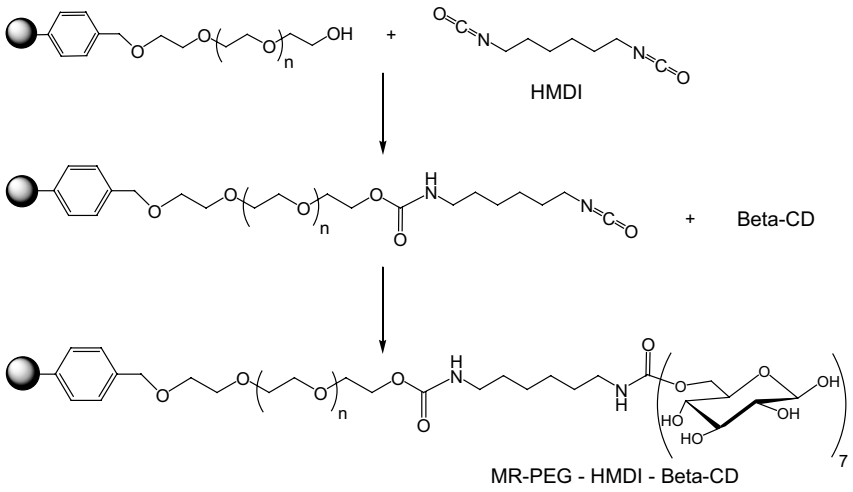

Figure 1. Immobilization of β-cyclodextrin on PEGylated Merrifield resin.

Table 1. Elemental analysis[10] of PEGylated MR and resin bound β-CD

Experiments	% O	% N	$Yield_{Obs}$ (g)	% Yield[d]	% Attachment[e]	Loading ($\times 10^{-3}$ mmol/g resin)
PEG_{200}-MR	5.85	0.0	5.949	89.3	59.3	737
$MRPEG_{200}$–HMDI	Nd[a]	Nd	3.342	99.4	90.3	598
$MRPEG_{200}$–HMDI–CD[b]	Nd	Nd	0.908	62.8	8.1	45.0
$MRPEG_{200}$–HMDI–CD[c]	8.34	1.79	1.146[f]	62.3	6.0	34.3

[a] Not determined.
[b] Microwave.
[c] Conventional.
[d] Based on weight.
[e] % Attachment = (weight $gain_{observed}$/weight $gain_{theory}$) × 100.
[f] Yield based on elemental analysis was 1.145 g.

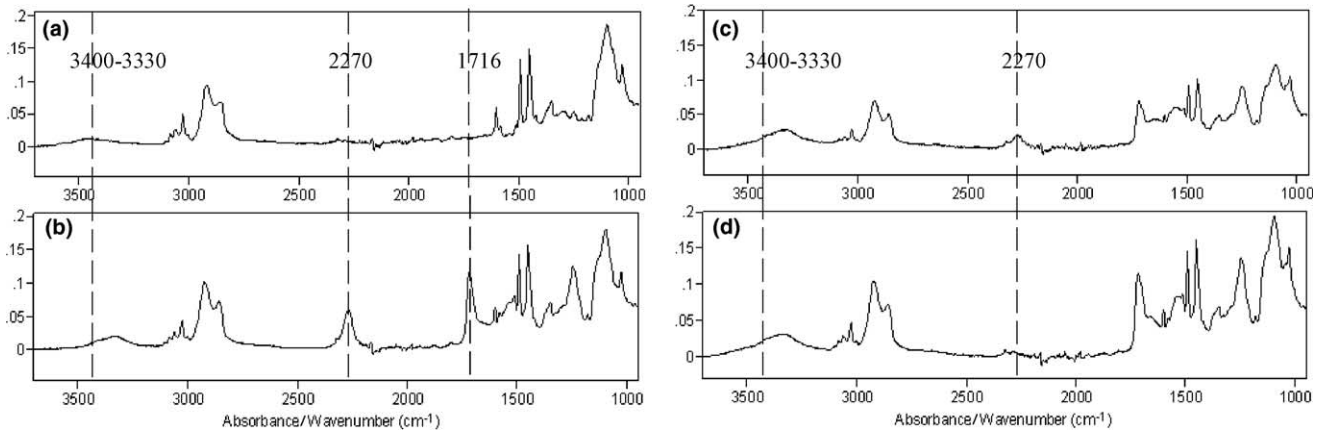

Figure 2. FT-IR spectrum of (a) MRPEG; (b) MRPEG–HMDI; (c) MRPEG–HMDI–CD (conventional); (d) MRPEG–HMDI–CD (microwave-assisted).

that the reaction under microwave irradiation has gone to completion due to the disappearance of the isocyanate group (Fig. 2d). However, despite similar yields, microwave-assisted process represents an overwhelming savings in time of reaction from 24 h to 30 min. The low yields obtained in this step may suggest possible deactivation of the terminal isocyanate group (see Table 1).

Furthermore, due to the well known property of β-cyclodextrin to form inclusion complexes with various compounds, we have also tested the ability of the resin bound β-cyclodextrin to remove volatile organic compounds from water. A standard VOC mixture[11] (0.4 ppm) was prepared in deionized water. Our study used HS/GC method[12] to analyze the volatile compounds remaining in the mixture, after passing through a column packed with the cyclodextrin trap. Table 2 shows the result from the trapping experiments. According to this table, just passing the sample through an empty pipette (blank) removes 58.4% of

Table 2. Retention of volatile organic compounds after resin treatments

	Volatile organic compound[a]											Total VOCs	SD[b]
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**		
	Area (pA/s)												
VOC without treatment	185.8	213.0	241.7	158.7	172.2	344.5	147.0	145.9	151.2	109.2	151.0	2019.9	35.6
Blank experiment	124.5	118.7	150.4	77.3	105.6	189.8	68.3	92.9	97.8	44.4	110.4	1179.9	43.1
Control—MRPEG	63.9	69.7	104.9	53.0	51.6	73.4	56.5	27.0	25.4	25.1	43.2	593.4	194.3
Sample—MRPEG–HMDI–CD	50.3	58.3	95.5	35.8	29.9	31.3	12.9	2.6	0.0	0.0	19.5	335.8	31.3

[a] VOCs: (1) chlorobenzene; (2) *p*-xylene; (3) *o*-xylene; (4) isopropylbenzene; (5) *n*-propylbenzene; (6) 2-chlorotoluene, (7) 4-chlorotoluene; (8) *tert*-butylbenzene; (9) *sec*-butylbenzene; (10) 1,3-dichlorobenzene; and (11) 1,4-dichlorobenzene.
[b] Standard deviation, based on two replicate experiments.

the volatiles. Taking this fact into consideration, the control material (resin without CD) was able to adsorb 29.3% (after correction for the blank) of the VOCs, whereas the resin with bound CD was able to trap 60.1% (after correction for the blank) of the VOCs. Considering relatively low % loading of CD, these values indicate a high efficiency of trapping. The VOCs could be thermally desorbed from the polymers for identification.

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9. Infrared spectra of the resins were acquired on a Bio Rad Excalibur FT-IR spectrometer equipped with a Golden Gate single reflection diamond ATR sampling device. A total of 128 scans at a resolution of 4 cm^{-1} were co-added.
10. Elemental analysis was performed by Guelph Chemical Laboratories Ltd (Guelph ON, Canada). Data reported are the average of duplicate measurements.
11. SS EPA Volatile organic compound mix 1—Supelco cat no. 48775/4S8775, Lot. LA-97831—contains 2000 ug/mL of each of the following components in methanol: chlorobenzene, isopropylbenzene, *n*-propylbenzene, *o*-xylene, *p*-xylene, *sec*-butylbenzene, *tert*-butylbenzene, 1,2-dichlorobenzene, 1,3-dichlorobezene, 1,4-dichlorobenzene, 2-chlorotoluene, 4-chlorotoluene.
12. In a typical experiment, the β-CD trap (~0.50 g) was packed in a pasteur pipette plugged with glass wool, then 11 mL of the VOCs solution (0.4 ppm, prepared in deionized water) was passed through the column and was collected in a 20 mL headspace vial. The vial was quickly capped and was transferred to the headspace sample cavity. Same procedure was carried out for the blank (with no sample and 10 mL of VOCs solution was used instead) and the control was packed with MRPEG resin. A Hewlett–Packard 7694E Headspace (HS) sample interfaced to a Hewlett–Packard 6890 GC was used for the HS/GC analysis of the VOCs. The vial was equilibrated at 80 °C for 15 min in the HS sample cavity. The loop filled for 0.1 min and was equilibrated at 90 °C, subsequently the volatiles were transferred at 100 °C and was injected at 150 °C into the GC column (HP-1, 30 m × 0.53 m × 0.88 m) with helium as the carrier gas. The GC column flow rate was set at constant pressure of 10.6 psi and the temperature was set at 80 °C for 10 min. The FID temperature was set at 280 °C.