

Preparation and Sorption Properties of Tunable Polyester Copolymers Containing β -Cyclodextrin

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ABSTRACT: Polyester copolymers were prepared with β -cyclodextrin (β -CD) and sebacoyl (SCI) or terephthaloyl (TCl) chloride cross linker agents using a simple, one-pot synthesis. Variation of the mole ratios (i.e., 1 : 1, 1 : 2, 1 : 3, 1 : 6, and 1 : 9) of β -CD to diacid chloride linker units resulted in copolymers with differing solubility and chemical stability in aqueous solution. The sorption properties of copolymers such as 1 : 6 and 1 : 9 SCI, and 1 : 9 TCl materials were investigated because of their relative insolubility and resistance to hydrolysis at pH 4.6. The monolayer sorption capacity (Q_m) of the copolymers varied according to the nature of the cross linker and the relative mole ratio of monomers. Q_m values obtained from the Sips isotherm model range from 2.7 to 5.2 mmol/g for the sorption of *p*-nitrophenol at 295 K and approach the value of Q_m for a commercially available granular activated carbon sorbent. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

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INTRODUCTION

α -, β -, and γ -cyclodextrins (CDs) are cyclic oligosaccharides containing 6-, 7-, and 8- α -D-glucopyranose units, respectively. In general, CDs have a lipophilic cavity interior and a hydrophilic exterior suitable for the inclusion of apolar guest molecules.¹ β -CD has a relatively low solubility in water (18.5 g/L), but modification of the hydroxyl groups by substituents at a variable degree of substitution results in CD derivatives with tunable solubility.¹ Hydroxypropyl-modified CDs have favorable solubility, biocompatibility, and drug delivery properties.² In contrast, polyurethane copolymers may be designed with tunable solubility and sorption properties. In the case of insoluble polyurethane copolymers containing CD comonomers, these materials have been investigated as sorbents for the treatment of wastewater.³ Modified CDs take advantage of the lipophilic CD cavity and the occurrence of host–guest interactions with various dyes,^{4,5} steroids,^{6,7} and lipophilic drugs.^{8,9} In contrast, the host–guest behavior of CD-based copolymers are less understood, particularly in the case of solid–solution equilibria. Insoluble CD copolymers have been prepared using cross linkers, such as diisocyanates and lactones, to form polyurethanes³ and polyesters.⁴

In the late 1920s, Carothers reported condensation reactions^{10,11} that would inspire the discovery of the common polyethylene

terephthalate polyesters used in the production of common plastic beverage bottles. These high-molecular-weight polyesters pose an environmental problem because of their resistance to chemical and biochemical degradation pathways.^{12–14} On the other hand, polyesters in various forms such as dendrimers¹⁵ and copolymers^{16,17} have been studied for use in drug delivery and as a biodegradable scaffolds for tissue engineering.¹⁸ Polyester-based materials which contain β -CD may possess variable solubility and chemical reactivity which depend on the nature of the cross linker and its crosslink density. Drug delivery applications that use polyester-based CDs were reported by Uekama et al.,¹⁴ where peracetylated β -CD copolymers were investigated with the vasodilating drug molsidomine. Cesteros et al.¹⁷ used a polyethylene glycol β -CD hydrogel as a sorbent for 1-naphthol. However, the issue of biodegradability and solubility in water has been a major obstacle in the application of CD-based polyesters for environmental applications. The use of aromatic linker units may stabilize the reactivity of the ester linkage through resonance; whereas, long-chain aliphatic linkers have been known to attenuate the rate of hydrolysis, especially as the chain length of the linker unit increases.¹⁹

The design of “smart” sorbent materials for applications for the controlled sorptive uptake of contaminants is feasible through tuning of the reaction conditions, the nature of the cross linker,

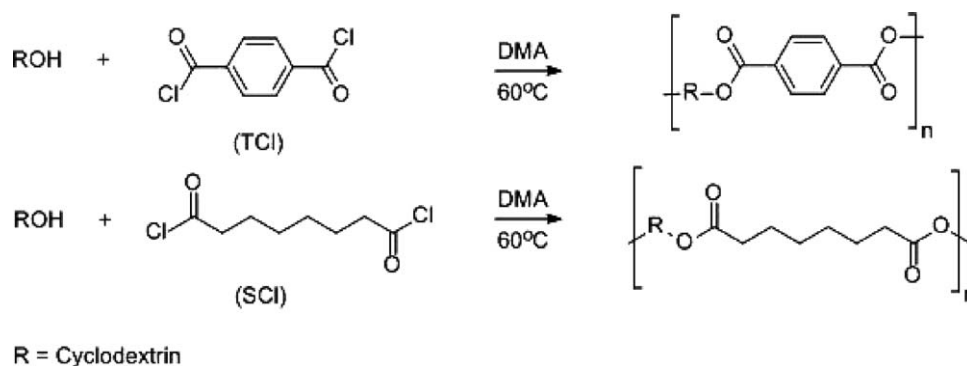


Figure 1. Polyester formation between cross linkers and the hydroxyl groups of β -CD; where R represents β -CD.

and the reactant ratios. In this article, the synthesis, characterization, and the sorption properties of polyester copolymers containing β -CD are described. Two types of linkers [sebacoyl (SCI) and terephthaloyl (TCl) chloride] were used to prepare copolymers with variable β -CD:linker mole ratio (1 : 1 to 1 : 9). In an effort to understand the potential application of such polyester copolymers as sorbents for environmental remediation, the sorption properties of the copolymers were studied with *p*-nitrophenol (PNP) in aqueous solution at 295 K and compared with granular activated carbon (GAC) using the Sips isotherm model.³

EXPERIMENTAL

Materials

β -CD and *p*-nitrophenol (PNP) were obtained from Alfa Aesar USA (Ward Hill, MA). Anhydrous dimethyl acetamide (DMA) was obtained from EMD (Edmonton, AB). The cross linker units TCl and SCI, sodium hydroxide, diphosphorous pentoxide, potassium phosphate monobasic, and solvents (acetone, methanol, and diethyl ether) were HPLC grade and obtained from Sigma–Aldrich Canada Ltd. (Oakville, ON). Granular activated carbon (GAC; Norit Rox 0.8) was obtained from Norit America and used as received. GAC materials were ground and sieved through a size 40 mesh (≤ 0.42 mm) particle sieve and subsequently dried under vacuum. The BET Surface area, as determined from multipoint BET analysis, was $951 \text{ m}^2/\text{g}$.²⁰ All other chemicals were used as received unless specified otherwise.

Apparatus

Fourier Transform IR-Spectra were obtained using a double beam spectrometer (Bruker, model Tensor 27). The sample chamber was purged with nitrogen gas, and solid samples were analyzed as KBr pellets in transmission mode. In the case of neat SCI (*l*), the sample was analyzed as a liquid film using a NaF cell. All samples were dried and stored in a desiccator before use.

NMR Spectroscopy: ¹H-NMR spectra were obtained at 500 MHz using a three-channel Bruker Avance (DRX) spectrometer with chemical shifts referenced internally using tetramethylsilane (TMS; $\delta = 0$ ppm). UV–vis absorbance spectra were obtained using a double beam Varian-Cary (Cary 100) spectrophotometer. Samples were analyzed in solution using quartz cuvettes.

Thermal gravimetric analysis (TGA) was carried out using a TA Instruments TGA (Q50). Nitrogen gas was used for cooling and purging of the sample compartment. Samples were analyzed in open aluminum pans over the temperature range between 30 and 500°C at a heating rate of $10^\circ\text{C min}^{-1}$.

Synthesis of β -CD:TCl and β -CD:SCI Copolymers

Before usage, β -CD and TCl were sieved and dried overnight in a pistol dryer with P_2O_5 as a desiccant. A combined mass of 2.0 g β -CD and TCl was used such that the mole ratios of β -CD to linker (1 : 1, 1 : 2, and 1 : 3) were obeyed. Once the β -CD and TCl (*s*) were under argon gas, 20 mL of anhydrous DMA was added to the round-bottomed flask with stirring until dissolved. The reaction was then heated to 60°C for 48 h, and the solvent was removed with vacuum until a gel-like phase was formed. The product was washed with a polar aprotic solvent such as acetone. A white to light yellow product was isolated using vacuum filtration and washed in a Soxhlet extractor with acetone for 48 h. After drying at 50°C in a vacuum oven, a second cycle of washing in the Soxhlet extractor with diethyl ether was carried out. In the case of 1 : 6 and 1 : 9 copolymers, methanol was used to replace acetone. Percent yields were calculated according to amount of β -CD and the respective amount of cross linker according to Figure 1. The reaction time needed to obtain the purified product did not exceed 1 week to minimize any hydrolysis. The identity of the copolymer products was supported by the accompanying ¹H-NMR results illustrated in Table I, in accordance with the identity of the various nuclei in Figure 2.

Solubility Measurements and Hydrolysis Test

A gravimetric approach was used to determine the solubility of the copolymers in deionized and distilled water (resistivity at 25°C $\sim 18.2 \text{ }\Omega\text{cm}$). Approximately, 60–100 mg of copolymer was added to a vial and 7.00 mL of water was then added. The mixture was equilibrated on a shaker table for 24 h. The copolymer was isolated using a centrifuge. A total of 1.00 mL of the supernatant solution was added to a preweighed sample vessel. After gentle drying at 50°C, the vessel was weighed and the gravimetric difference used to calculate the solubility.

Hydrolysis of the polyester copolymers was evaluated using the above procedure in aqueous buffer solution (0.10 mM KH_2PO_4 buffer at pH = 4.6 or 0.10 mM NaHCO_3 buffer at pH = 9.0). A total of 3M NaOH was used to adjust the pH of the buffer

Table I. ¹H-NMR Data for TCI/SCI Copolymers and Comonomers in DMSO-*d*₆ at 500 MHz and 295 K

	H ₁ (ppm)	H ₂ -H ₇ (ppm)	OH ₆ (ppm)	OH ₂ ,OH ₃ (ppm)	H ₁₁ (ppm)	H ₁₂ (ppm)	H ₁₃ (ppm)	H _{ar} (ppm)
β-CD hydrate	4.83, s, 7	3.32-3.65, m, 42	4.46, t, 7	5.70, m, 14	NA	NA	NA	NA
SCI	NA	NA	NA	NA	2.30, t, 4	1.50, t, 4	1.25, s, 8	NA
1 : 1 SCI	4.83, m, 7	3.32-3.60, m, 42	4.46, m, 6	5.54, s, 14	2.30, m, 8	1.50, s, 8	1.25, s, 16	NA
1 : 2 SCI	4.84, m, 7	3.32-3.60, m, 42	4.46, m, 2	5.54, s, 14	2.30, m, 12	1.50, s, 12	1.25, s, 24	NA
1 : 3 SCI	4.84, m, 7	3.32-3.60, m, 42	4.46, m, 7	5.54, s, 14	2.30, m, 16	1.50, s, 16	1.25, s, 32	NA
1 : 6 SCI	4.84, m, 7	3.32-3.60, m, 42	4.46, m, 7	5.54, s, 14	2.30, m, 30	1.50, s, 30	1.25, s, 56	NA
^a TCI	NA	NA	NA	NA	NA	NA	NA	8.25, s, 4
1 : 1 TCI	4.83, m, 7	3.32-3.60, m, 28	4.46, m, 6	5.54, s, 14	NA	NA	NA	8.07, m, 4
1 : 2 TCI	4.84, m, 7	3.32-3.60, m, 28	4.46, m, 2	5.54, s, 14	NA	NA	NA	8.10, m, 8
1 : 3 TCI	4.84, m, 7	3.32-3.60, m, 28	4.46, m, 7	5.54, s, 14	NA	NA	NA	8.07, m, 14

The chemical shifts are relative to TMS ($\delta = 0$ ppm) where the multiplicity, and integrated peak areas are indicated.

s, singlet, t, triplet, and m, multiplet.

NA, not applicable.

^aTCI NMR solvent was CDCl₃ relative to TMS ($\delta = 0$ ppm).

solutions, and the salt content of the buffer was accounted for in the determination of copolymer solubility results.

Sorption Measurements

The molar absorptivity (ϵ) of *p*-nitrophenol (PNP) was estimated using a Beer-Lambert calibration plot ($\lambda_{\max} = 318$ nm; $\epsilon = 10,176$ L mol⁻¹ cm⁻¹) at pH = 4.6, in agreement with the literature.³ Deviations from the Beer-Lambert law occur when [PNP] > 0.18 mM; therefore, the supernatant solution from the solid-solution sorption equilibria was analyzed within the linear region and diluted accordingly. The sorption of PNP was carried out for copolymer products with negligible solubility and hydrolysis at pH 4.6, as outlined above. In a typical sorption experiment, 20.0 ± 0.2 mg of copolymers (GAC: 2.0 ± 0.2 mg) were added to each of the 15 vials. A series of vials without sorbent were used as blanks. A stock solution of PNP in 0.10 mM KH₂PO₄ buffer at pH = 4.6 was serially diluted over a range of concentrations (0.6–60.0 mM), as required. A total of 7.00 mL of PNP solution at variable concentration was added to each vial containing sorbent and blank. The samples were mixed on a shaker table for 24 h at 295 K, and the absorbance of PNP was measured quantitatively using UV-vis spectrophotometry, as outlined above.

Data Analysis

The isotherm results were expressed as plots of the amount of PNP adsorbed per mass of sorbent (Q_e) against the residual equilibrium concentration of PNP in aqueous solution using eq. (1).

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

C_0 and C_e are the initial and final concentrations (mol/L) of PNP before and after sorption, respectively. V is the volume (mL) of the dye solution and m is the mass (g) of sorbent.

The sorption isotherms were analyzed using the Sips model [cf. eq. (2)] which accounts for behavior described by the Freundlich and Langmuir isotherms at certain limiting conditions.²¹

$$Q_e = Q_m \left[\frac{K_s(C_e^n)}{(1 - K_s(C_e^n))} \right] \quad (2)$$

The terms Q_e and C_e in eq. (2) are defined by eq. (1). Q_m , K_s , and n represent the adjustable fitting parameters. The sorbent-adsorbate binding affinity can be related to the equilibrium constant (K_s) and the adjustable exponent parameter (n), and Q_m is the monolayer sorption capacity (mmol/g). Langmuir behavior is predicted when $n_s = 1$, whereas Freundlich behavior occurs when $K_s C_e^{n_s} < 1$.

A comparison of the goodness-of-fit between the experimental and calculated (i.e., Sips model) Q_e values was estimated using R^2 and the root mean square error (RMSE) to determine if favorable agreement was obtained.

$$\text{RMSE} = \sqrt{\frac{\sum(Q_e - Q_T)^2}{N}} \quad (3)$$

$$R^2 = 1 - \frac{\sum(Q_e - Q_T)^2}{\sum(Q_e - Q_{Av})^2} \quad (4)$$

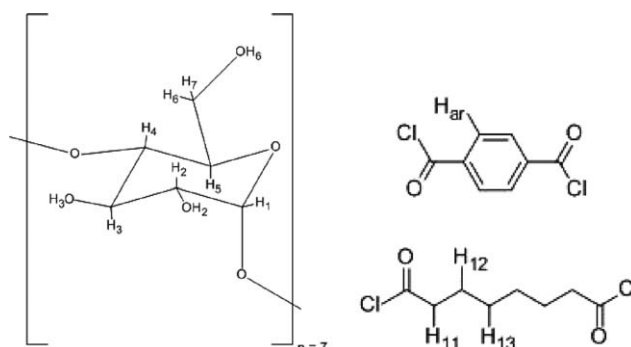


Figure 2. ¹H-NMR labeling scheme for the ¹H nuclei of β-CD and cross linkers. Left: A monomer of β-CD; Right: The bifunctional cross linkers; SCI and TCI.

Table II. Product Yields for Copolymers According to the Reaction Scheme in Figure 1

Copolymer	Yield (%) copolymer	Copolymer	Yield (%) Copolymer
1 : 1 SCl	69	1 : 1 TCl	51
1 : 2 SCl	70	1 : 2 TCl	80
1 : 3 SCl	64	1 : 3 TCl	66
1 : 6 SCl	40	1 : 6 TCl	50
1 : 9 SCl	70	1 : 9 TCl	66

Q_e is the experimental sorption capacity [cf. eq. (1)] and Q_T is the calculated sorption capacity according to the Sips isotherm [cf. eq. (2)] based on the best-fit adjustable parameters (i.e., Q_m , K_s , and n). Q_{Av} is the average experimental sorption capacity and N is the number of data points.

RESULTS AND DISCUSSION

Synthesis and Characterization of Copolymers

The synthesis of the polyester copolymers described by Figure 1 was adapted from a previous study³ that reported copolymers with tunable properties by varying the relative mole ratios of β -CD and the cross linker units. The identity of the copolymer products is supported by the ¹H-NMR results in Table I, in accordance with the numbering system defined by Figure 2.

The product yields are favorable according to Table II and are relatively unaffected by the presence of residual water in the reaction mixture. In some cases, the reduced yields are related to the loss of product in the isolation and purification steps because of losses during filtration. Given that HCl is a by-product from the reaction, the basicity of the solvent is anticipated to affect the product yields due to attenuation of potential acid hydrolysis of the copolymers. DMA is considered a weak base ($pK_a = 0.19$), whereas triethylamine is a more basic solvent and was used previously.²² DMA was chosen as the most appropriate solvent because of the favorable solubility of each comonomer required for the synthesis.

The structural characterization and thermal analyses of the copolymers were carried out using spectroscopic (FTIR and ¹H-NMR) and TGA methods. Direct evidence supporting the product identity is provided by the NMR and IR results (cf. Table I and III) for the copolymers. The carbonyl vibrational band observed in the range of 1683–1727 cm^{-1} (TCl-based copolymers) and 1725–1745 cm^{-1} (SCl-based copolymers) are consistent with the spectral region for ester functional groups.²²

In a previous report,¹⁸ an increase in the cross linker content results in a decreased intensity of the hydroxyl signature of β -CD due to increased substitution of its annular hydroxyl groups. Each bifunctional cross linker reacts with two hydroxyls of β -CD (cf. Figure 1). The intensity effect can be seen in Figure 3 by comparing the relative intensities of the carbonyl and hydroxyl vibrational bands. As the β -CD:linker mole ratio approaches 1 : 6, the intensity of the hydroxyl signature

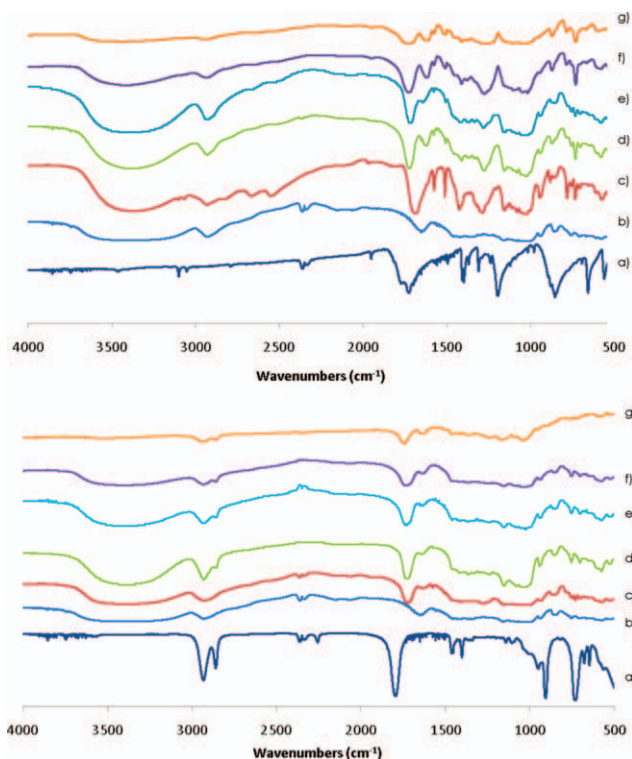


Figure 3. Top: FTIR Spectra of TCl copolymers and initial reagents. (a) TCl, (b) β -CD, (c) 1 : 1 TCl, (d) 1 : 2 TCl, (e) 1 : 3 TCl, (f) 1 : 6 TCl, and (g) 1 : 9 TCl. Bottom: FTIR Spectra of SCl copolymers and initial reagents. (a) SCl, (b) β -CD, (c) 1 : 1 SCl, (d) 1 : 2 SCl, (e) 1 : 3 SCl, (f) 1 : 6 SCl, and (g) 1 : 9 SCl. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

decreases relative to the carbonyl band, in accordance with the formation of ester linkages.

For the comonomer ratio 1 : 9, the intensity of the signature of the hydroxyl band reaches a minimum for this copolymer. Again, this suggests further crosslinking. From Table III, the decrease in the wave number value for the carbonyl band of the acyl chlorides at 1772 cm^{-1} (TCl) and 1796 cm^{-1} (SCl) to 1683–1727 cm^{-1} for the TCl copolymers, and 1725–1745 cm^{-1} for the SCl copolymers, provide strong support of the formation of ester linkages.²² The intensity of the aromatic ring bending modes $\sim 1624 \text{ cm}^{-1}$ provides support of copolymer formation. As the TCl content of the copolymer increases, the intensity of the C—C skeletal bands increased relative to the aliphatic C—H bands $\sim 2930 \text{ cm}^{-1}$ for β -CD.

Comparison of the spectra for TCl and its copolymers reveals a narrowing of the carbonyl band for the monomeric cross linker relative to the copolymer products. The broadening disappears and the carbonyl bands sharpen for the copolymer materials. The decrease in the ring bending band for the TCl copolymers ($\sim 1650 \text{ cm}^{-1}$) are attributed to ester formation and the corresponding electronic effects of the arene ring of the linker unit. Similar observations are noted for the SCl copolymers (cf. Figure 3) for the C—C skeletal bands of the linker unit. The IR results presented above are consistent with the molecular identity of polyester copolymers.

Table III. Wave number Values for Selected IR Signatures of TCl- and SCl-Based Copolymers and Comonomers

	C—H ring bending	C—O stretches	CH ₂ and CH asymmetric bending	C—C skeletal	C=O asymmetric stretch	C—H stretch	O—H stretch
β-CD hydrate	576	1027	1418	1653	NA	2927	3394
	706						
	756						
SCl ^a	NA	NA	1465	NA	1796	2858 2931	NA
1 : 1 SCl	578	1029	1418	1645	1725	2861	3412
	706					2931	
	756						
1 : 2 SCl	578	1030	1412	1653	1732	2859	3396
	706					2931	
	756						
1 : 3 SCl	580	1031	1413	1649	1733	2859	3384
	706					2930	
	756						
1 : 6 SCl	578	1028	1416	1639	1737	2858	3403
	706					2931	
	755						
1 : 9 SCl	577	1043	1417	1630	1745	2857	3540
	725					2932	
	764						
TCl	854	NA	1408	1653 [†]	1772	3053	NA
	656					3100	
1 : 1 TCl	573	1029	1424	1683 ^{a, b}	1683	2930	3375
	733						
	872						
1 : 2 TCl	580	1027	1410	1624 ^b	1723	2929	3385
	731						
	873						
1 : 3 TCl	580	1027	1411	1623 ^b	1721	2929	3377
	731						
	874						
1 : 6 TCl	580						
	730						
	873	1017	1411	1622 ^b	1726	2934	3409
1 : 9 TCl	600	1017	1411	1622 ^b	1727	2939	3428
	730						
	873						

All wave numbers are in cm⁻¹ units.

^aAnalyzed as a liquid film, as outlined in the experimental section, ^bIncludes the aromatic ring-bending mode for the TCl linker.

¹H-NMR Spectroscopy

In Figures 4 and 5, the ¹H-NMR spectra for the resonance lines of β-CD (~3.3 to 3.7 ppm) are broadened as the linker content of the copolymer increases. This is attributed to the reduced motional dynamics of the β-CD monomers with increasing crosslink density of the copolymer, in agreement with a previous report.¹⁸ Table IV lists the integration results of selected

nuclei of β-CD and the cross linker units at variable monomer ratios. The integration of the aromatic nuclei of TCl (H_{ar}) and methylene groups (H₁₂) of SCl relative to various nuclei of β-CD afford estimates of the relative comonomer composition of the copolymer. At the 1 : 1 mole ratio for the TCl copolymer, there are 4 H₁₁ nuclei of TCl per 7 H₁ nuclei of β-CD. A comparable scaling ratio is observed for the 1 : 2 copolymer of SCl,

for the relative intensity ratios of H_{12} and H_1 nuclei (cf. Figure 2). The calculated values are in good agreement with the stoichiometric feed ratios of the monomers used in the synthesis (cf. Figure 1). In the case of copolymers prepared at higher ratios (i.e., 1 : 6 TCl, 1 : 9 SCl, and 1 : 9 TCl), the copolymer products were relatively insoluble for the solvents investigated, and their quantitative analysis was precluded (cf. Table IV) using solution $^1\text{H-NMR}$ spectroscopy.

Because polyester materials are known to undergo hydrolysis, it is useful to determine the pH conditions where hydrolysis may occur. The $^1\text{H-NMR}$ spectra in Figure 6 illustrate that the 1 : 3 SCl copolymer undergoes hydrolysis at basic conditions and appears to be more stable in D_2O at ambient pH conditions. Similar observations were noted for the 1 : 3 TCl copolymer (results not shown). The hydrolysis of the copolymer is evidenced according to the sharpening of the broad resonance lines of the copolymer upon addition of base. As well, there is a pronounced sharpening of the nuclei corresponding to SCl ($\sim 0.7\text{--}2.5$ ppm) and $\beta\text{-CD}$ ($\sim 3.5\text{--}4$ ppm) with upfield chemical shifts for the $\alpha\text{-CH}_2$ groups of SCl. Hydrolysis occurs for the 1 : 3 SCl and TCl copolymers in solution at pH 4.6. The copolymers prepared at greater mole ratios ($> 1 : 6$) undergo attenuated hydrolysis and display properties more suitable as solid phase sorbents in aqueous solution at pH 4.6.

Thermal Gravimetric Analysis

Decreased solubility and attenuated hydrolysis were observed as the linker content of the copolymer increases. The effect is related to the reduced solvation of the ester linkage due to steric effects resulting from increased substitution of the annular hydroxyl groups of $\beta\text{-CD}$. Mohamed et al.²³ independently identified the occurrence of steric effects with increasing cross linker content for urethane copolymers containing $\beta\text{-CD}$.

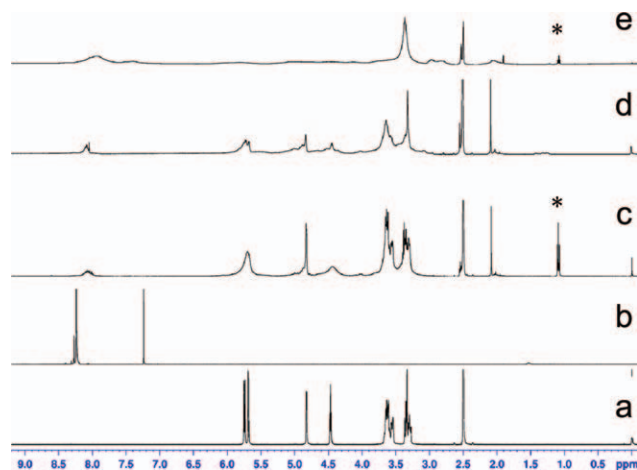


Figure 4. $^1\text{H-NMR}$ spectra of selected TCl copolymer products; (a) $\beta\text{-CD}$, (b) TCl, (c) 1 : 1 TCl, (d) 1 : 3 TCl, and (e) 1 : 6 TCl. All spectra were obtained in $\text{DMSO-}d_6$ except for the reagent TCl which is obtained in CDCl_3 , and chemical shifts were referenced to TMS. *Note that the triplets observed at 1.09 ppm is residual diethyl ether. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

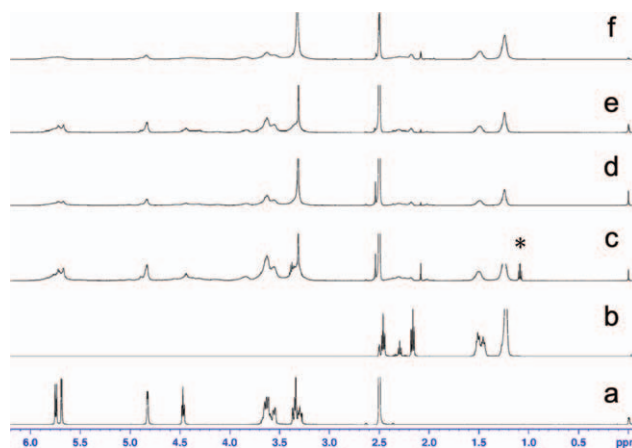


Figure 5. $^1\text{H-NMR}$ spectra of SCl and its copolymer materials at 295 K in $\text{DMSO-}d_6$ at 500 MHz. (a) $\beta\text{-CD}$, (b) SCl, (c) 1 : 1 SCl, (d) 1 : 2 SCl, (e) 1 : 3 SCl, and (f) 1 : 6 SCl. All spectra were obtained in $\text{DMSO-}d_6$ where chemical shifts are referenced to TMS. *Note: The triplets at 1.09 ppm is residual diethyl ether. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In Table V and Figure 7, the TGA results for the copolymers and the comonomers are provided. In general, two transitions are observed, and are attributed to thermal decomposition processes of the copolymer framework, according to dissociation of the respective monomer subunits, cross linker, and βCD . The assignment of TGA transitions are consistent with the results reported for urethane copolymers.²⁴ The decomposition temperature of $\beta\text{-CD}$ in its monomer form and its copolymer form may vary up to $\sim 45^\circ\text{C}$ (cf. Table V) according to the nature of the linker and the relative $\beta\text{-CD}$:linker ratio. The SCl-based copolymer appears to have greater thermal stability relative to the TCl-based copolymers. Different thermal stabilities are related to conformational effects of each linker unit because it affects the relative heat capacity of the copolymer materials. Differences in the framework flexibility are supported by the differences in the swelling behavior of copolymers containing aliphatic- and aromatic-based linkers. The greater conformational motility of SCl contributes to enhanced thermal stability according to the greater conformational degrees of freedom of SCl, relative to the relatively rigid TCl unit. The greater thermal stability observed for SCl copolymers is evidenced by the substantial thermal stability of the 1 : 9 SCl copolymer, and exceeds that of all the copolymers investigated herein. The potential occurrence of self-inclusion of the SCl aliphatic linker may also contribute, in part, to enhanced thermal stability since such types of host-guest interactions have been previously reported.²

A noteworthy result is the temperature stability shift for the 1 : 6 and 1 : 9 copolymers containing SCl and TCl. In Table V, the respective copolymers have different framework structural characteristics as compared with copolymers with reduced crosslink density (i.e., 1 : 1, 1 : 2, and 1 : 3 TCl). The lower thermal decomposition temperature for the latter is a measure of the reduced thermal stability. As the linker content increases, the intensity of the peak $\sim 139^\circ\text{C}$ for the TCl copolymers decrease and may be related to the formation of more densely cross

Table IV. ^1H -NMR Results of Selected Copolymer Nuclei in Solution at 295 K

	Chemical shift of interest (ppm, DMSO- d_6)	Integration	Calculated mole ratio via NMR (value in brackets not rounded to the nearest integer)
1 : 1 TCl	4.83, m	7.00	1 : 1 (1 : 1.1)
	8.00, m	4.54	
1 : 2 TCl	4.83, m	7.00	1 : 2 (1 : 2.4)
	8.00, m	9.70	
1 : 3 TCl	4.83, m	7.00	1 : 4 (1 : 3.8)
	8.00, m	15.14	
1 : 1 SCl	4.84, m	7.00	1 : 2 (1 : 1.7)
	1.52, m	6.91	
1 : 2 SCl	4.84, m	7.00	1 : 2 (1 : 2.2)
	1.52, m	9.00	
1 : 3 SCl	4.84, m	7.00	1 : 4 (1 : 4.2)
	1.52, m	16.86	
1 : 6 SCl	4.84, m	7.00	1 : 5 (1 : 4.5)
	1.52, m	17.98	

^1H nuclei: (H_1 ; β -CD), (H_{11} ; TCl), and (H_{12} ; SCl).

linked materials. As the linker content of the SCl copolymers increase, the peak corresponding to β -CD $\sim 318^\circ\text{C}$ shifts to a higher temperature $\sim 358^\circ\text{C}$ (cf. Figure 7).

Solubility Measurements

The linker units are apolar relative to the hydrophilic regions of β -CD. Increased cross linking and substitution of the annular hydroxyl groups of β -CD reduce the accessibility of solvent, copolymer solubility, and hydrolysis of the copolymer. These effects are observed according to the reduced solubility (cf. Table VI) of the copolymers as the β -CD:linker mole ratio approaches 1 : 6, in accordance with increased cross linking. The greater solubility for TCl copolymers when compared with SCl copolymers may be due to differences in the relative solvent accessibility for each copolymer. The rigid nature of TCl lowers its conformational flexi-

bility, relative to SCl, because SCl may undergo substantial conformational changes in aqueous solution. The solubility values of the copolymer may be overestimated due to the hydrolysis of such polyesters, as outlined above. Aromatic linkers may exhibit a resonance effect on the carbonyl group, increasing the reactivity

Table V. TGA Decomposition Temperature Results of SCl and TCl Copolymers

Sample	Decomposition temperature ($^\circ\text{C}$)	Sample	Decomposition temperature ($^\circ\text{C}$)
β -CD hydrate	314.0	TCl	139.6
1 : 1 SCl	311.0	1 : 1 TCl	212.1, 284.6
1 : 2 SCl	302.3	1 : 2 TCl	215.4, 271.7
1 : 3 SCl	313.5	1 : 3 TCl	279.3
1 : 6 SCl	313.8	1 : 6 TCl	274.6, 297.5
			326.2
1 : 9 SCl	358.1	1 : 9 TCl	278.5, 298.8

Table VI. Solubility Results for the Copolymers in Water at 295 K

Sample	Solubility (g/L)	Sample	Solubility (g/L)
1 : 1 TCl	12.5	1 : 1 SCl	7.00
1 : 2 TCl	7.07	1 : 2 SCl	6.66
1 : 3 TCl	6.22	1 : 3 SCl	4.06
1 : 6 TCl	0.24	1 : 6 SCl	0.19
1 : 9 TCl	0.51	1 : 9 SCl	ND ^a
B-CD Pure	18.5		

^aThis value was not determined.

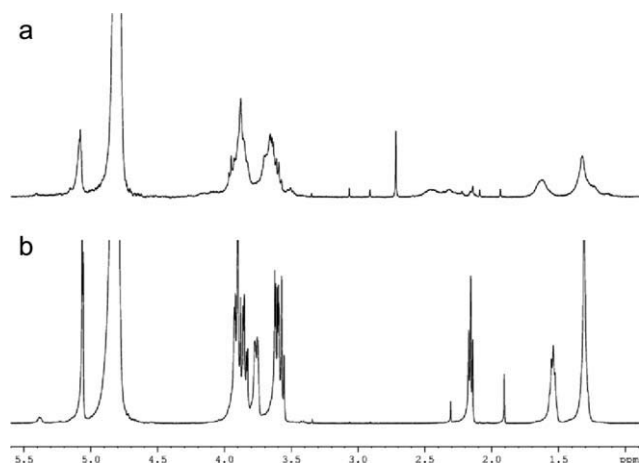


Figure 6. ^1H -NMR spectra in D_2O at 295 K: (a) 1 : 3 SCl and (b) 1 : 3 SCl after addition of one drop of 3M NaOH.

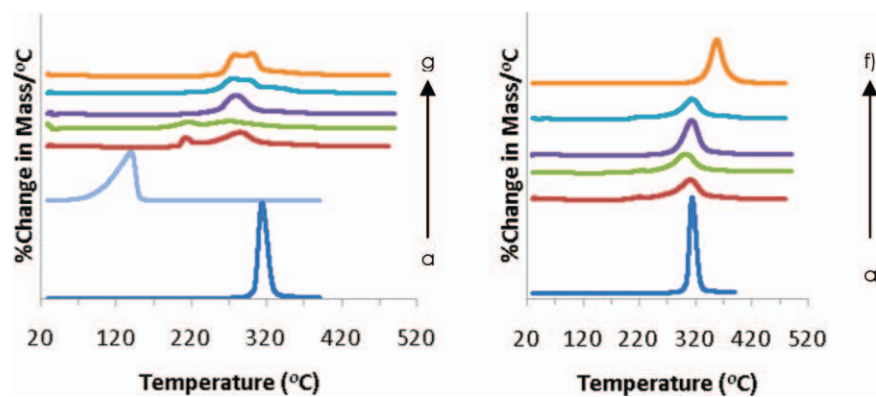


Figure 7. Left: TGA spectra of TCl copolymers and initial reagents. (a) β -CD, (b) TCl, (c) 1 : 1 TCl, (d) 1 : 2 TCl, (e) 1 : 3 TCl, (f) 1 : 6 TCl, and (g) 1 : 9 TCl. Right: Thermograms of SCl copolymers and comonomer reagents. (a) β -CD, (b) 1 : 1 SCl, (c) 1 : 2 SCl, (d) 1 : 3 SCl, (e) 1 : 6 SCl, and (f) 1 : 9 SCl. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the ester linkage to hydrolysis, when compared with aliphatic polyesters. In turn, the aromatic linker exhibits greater hydrolysis of such copolymer materials. In contrast, SCl copolymers may undergo coiling of the methylene chain, attenuating access of solvent into the micropores of the copolymer framework, and reduced hydrolysis.

Sorption Isotherms

Solubility was measured at pH 9.0 and pH 4.6, respectively. The copolymers that did not hydrolyze at pH 4.6 were 1 : 6 TCl, 1 : 9 SCl, and 1 : 9 TCl. All other copolymers undergo hydrolysis at pH 9.0, whereas the hydrolysis of the 1 : 9 TCl and 1 : 9 SCl copolymers were attenuated. The 1 : 6 SCl copolymer undergoes

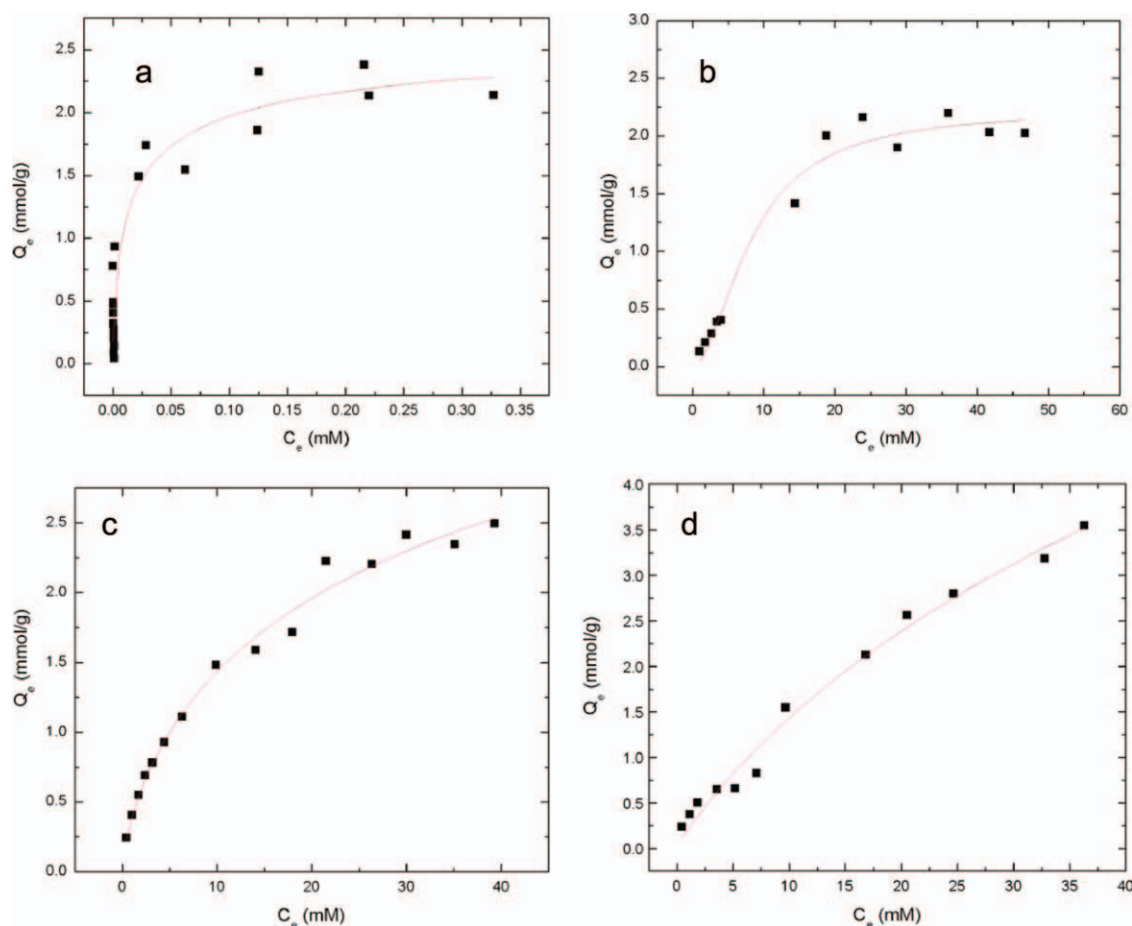


Figure 8. Sorption isotherms of PNP at pH = 4.6 and 295 K in aqueous solution. (a) GAC, (b) 1 : 6 TCl, (c) 1 : 9 SCl, and (d) 1 : 9 TCl. The solid lines represent the best fit, according to the Sips isotherm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table VII. Sips Sorption Parameters for Various Copolymer Materials and PNP at pH = 4.6 and 295 K in Aqueous Solution

Sample	Q_m (mmol/g)	K_s	N	R^2	RMSE
GAC	2.70	10.6	0.592	0.901	0.472
1 : 6 TCl	2.23	0.0146	1.78	0.977	1.11
1 : 9 TCl	5.16	0.0821	0.671	0.988	0.871
1 : 9 SCl	11.1	0.0195	0.885	0.986	0.763

partial hydrolysis at pH 4.6 since most of the copolymer remains after several days of mixing, enabling evaluation of the sorption properties with PNP in aqueous solution at pH 4.6. Figure 8 illustrates the sorption isotherms of the various copolymers with PNP at 295 K. According to Figure 8, the equilibrium dye concentration (C_e) increases until saturation of the sorption sites are reached. As the mole content of the linker increases, the sorption capacity of the copolymer increases, as noted with other copolymer materials containing β -CD.³ A comparison of the sorption capacity of the three polymers with GAC ($Q_m = 2.70$ mmol/g) illustrates important differences in their sorption properties (cf. Table VII). The 1 : 9 SCl copolymer has a sorption capacity (11.1 mmol/g) and exceeds that of activated carbon. The 1 : 6 TCl (2.23 mmol/g) and 1 : 9 TCl (3.06 mmol/g) copolymers show comparable sorption relative to GAC. The average monolayer sorption capacity (Q_m) of polyurethane/ β -CD copolymers (1.0 mmol/g)³ and epichlorohydrin/ β -CD copolymers (0.5 mmol/g)²⁵ are lower than the reported Q_m values for the polyesters herein.

The sorption isotherms for GAC, 1 : 6 TCl, and 1 : 9 TCl are considered more reliable than the results for the 1 : 9 SCl copolymer because of their relative insolubility and resistance to hydrolysis. A type IV isotherm is seen for 1 : 9 SCl (cf. Figure 8) where a plateau occurs $\sim C_e = 5$ –10 mM, indicating that sorption occurs onto a mesoporous framework structure.^{26,27} For the 1 : 6 and 1 : 9 TCl copolymers, the isotherm follows a type I adsorption profile characteristic of microporous materials. The difference between the two types of sorption may be due to the relative size effects and conformational behavior of the SCl and TCl linker units. The cross linker chain of SCl may undergo variable conformations from a coiled- to an all-trans form, affecting the relative accessibility of the β -CD sorption sites.^{27,28} Conformation effects are limited for the rigid aromatic TCl linker and affect accessibility of the β -CD sorption sites to a lesser degree. The potential coiling of the SCl linkers is anticipated to reduce the framework access of SCl copolymers relative to TCl copolymers. The Sips model parameters (cf. Table VII) provide estimates of the relative accessibility of the sorption sites according to the n -values for 1 : 9 SCl and 1 : 9 TCl copolymers. A comparison of the Sips isotherm parameter (n) for the 1 : 9 SCl copolymer with GAC indicates that the pores of the latter are not readily accessible²⁹ and display unfavorable energy relative to the copolymer. This may be related to the nonswelling characteristics and apolar nature of the carbonaceous framework of GAC. The Sips parameter, n , affects the distribution of sorption sites as a function of their energy of adsorption.¹⁷ As the n -value approaches unity, the distribution

of the sorption sites is reduced and the energy of all the adsorption sites become more uniform, and relate to the maximum adsorption corresponding to the fully accessible β -CD sites. The 1 : 9 SCl copolymer has an n -value ($n = 0.885$) exceeding that for 1 : 9 TCl ($n = 0.671$). The propensity of 1 : 9 SCl to undergo substantive conformational changes and swelling may contribute to its greater sorption site accessibility in the hydrated state. Thus, the energy of adsorption at those sites is more closely related to the fully accessible β -CD sites, in accordance with its greater n -value. The Sips isotherm assumes there are a finite number of sorption sites and monolayer adsorption occurs when n is unity.¹⁷ If multilayer sorption occurs (i.e., $n \neq 1$), similar to the BET model, the number of sorption sites are not finite as every adsorbed molecule forms a new sorption site. Overall, it appears that monolayer sorption occurs for the copolymers investigated herein. The observed deviations between the Sips model and the experimental data, according to eq. (4), may arise from errors in C_e due to hydrolysis as it contributes to negative errors in Q_e . Thus, the sorption properties of copolymers with greater linker content have lower solubility and attenuated hydrolysis, and more reliable sorption parameters.

CONCLUSIONS

In this article, we report the synthesis and characterization of polyester-based sorbent materials containing β -CD at various reactant ratios using two types of diacid chlorides (SCl and TCl chloride), respectively. The molecular identity of the products was confirmed using ¹H-NMR/FTIR spectroscopy and TGA.

The sorption properties of the copolymer materials were studied in aqueous solution using PNP as a model organic adsorbate at pH 4.60 and compared with GAC. The sorption isotherms are well described using the Sips isotherm. The ordering of the relative sorption capacity is given, as follows: 1 : 9 SCl > 1 : 9 TCl > 1 : 6 TCl > GAC. Therefore, the use of such materials for solid-phase extraction for wastewater treatment may be feasible in aquatic environments. The use of copolymers with variable cross link density with tunable properties (i.e., hydrolysis and sorption) offers an opportunity to develop "smart materials" for controlled-release of pharmaceuticals and remediation of phenolic contaminants aquatic environments.

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