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New Organic Nanoporous Polymers and Their Inclusion Complexes

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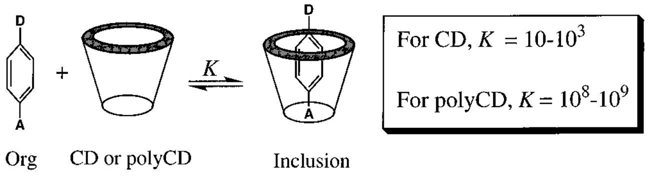
A class of cyclic glucopyranose oligmers from starch, cyclodexrins (CD), have a characteristic toroidal shape that forms a well-defined cylindrical cavity.[1] This cavity can include another organic compound with suitable geometry and polarity (Scheme 1). Indeed, long alkyl chains and aromatic compounds form inclusion complexes with cyclodextrins in water. However, inclusion formation constants[1−5] typically are $K' = 10-10^3$ M^{-1}. These weak noncovalent interactions are interesting but far from being useful in real-world applications such as reducing organic contamination in water to below parts per billion levels.

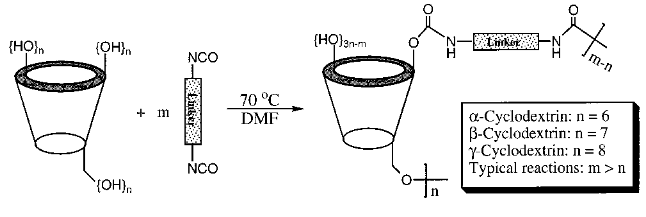
We have recently fabricated cyclodextrin polymers that exhibit an interconnected nanoporosity with a dramatically increased inclusion formation constant, $K \geq 10^8$ M^{-1} (Scheme 1 and 2). This is significant because a simple conversion from cyclodextrin monomers to nanoporous polymers could have such a dramatic effect on noncovalent interactions in aqueous solutions (Scheme 1). Previous studies on cyclodextrin polymers focus mostly on cross-linking cyclodextrin with epichlorohydrin[6,7] which is commercially available and has low binding constant to organics.[8] Studies using cyclodextrins to coat solid particles as a stationary phase for enantiomer separation were also reported.[9,10] Formation of inclusion complexes are rarely proven in these cyclodextrin polymers, including using cholesterol as a template to synthesize cyclodextrin polymers.[11]

The nanoporous polymers as granular solids, powders, and films are synthesized by reacting purified cyclodextrins with diisocyanato compounds with 1:8 molar ratio in dried DMF solution (Scheme 2). The diisocyanato compounds chosen are hexamethylene diisocyanate (HDI) and toluene 2,6-diisocyanate (TDI). While the clear solution of cyclodextrins and diisocyanates is heated to 70 °C for 16−24 h, white nanoporous materials are obtained with ~100% yield after removal of DMF.[12] The chemical conversion is monitored with infrared spectroscopy, which shows the complete disappearance of the isocyanato group at 2270 cm^{-1} and the growth of vibration bands at 3370, 1715, and 1530 cm^{-1}, corresponding to N−H, C=O, and NH−CO groups. Optical-quality films also can be fabricated at 70 °C by evaporating solvent in an atmosphere saturated with DMF solvent vapor pressure.

Scheme 1



Scheme 2



We examined the pore size of the cyclodextrin polymers and their selectivity using solute rejection methods in which molecules with a variety of structures and different sizes were selected to probe "nanoporosities." We chose solute molecules from two classes of water soluble compounds: phenol derivatives and organic sulfonate salts. Aqueous solutions containing these organics were passed through cyclodextrin polymer powders, and the maximum amount of organic guest molecules loaded into the polymers were determined by measuring the concentration difference in the solutions before and after the polymers with UV−vis spectroscopy. In general, we discovered that molecules with the right dimensions spontaneously entered the cyclodextrin cavities. For nitrophenol, we found first-order kinetics initially, $v = k_{+1a}C_{NP}S$, which then switched to zero-order kinetics, $v = k_{+1b}S$, where $k_{+1a} = 0.68$ h^{-1} m^{-2}, $k_{+1b} = 1.2 \times 10^{-2}$ M h^{-1} m^{-2}, S is the surface area, and C_{NP} is the nitrophenol concentration. As shown in Figure 1, molecules with linear rodlike feature will form inclusion complexes if the rod diameter is smaller than or close to the cyclodextrin cavity size. For α-cyclodextrin polymers, examples of these molecules, along with their assumed diameters in parentheses, are trichloroethylene (5.0 Å), toluene (5.1 Å), phenol (5.1 Å), 4-nitro(thiol)phenol (5.1 Å), 2,6-dimethyl-4-nitrophenol (7.4 Å), 2-nitro-1-naphthol (7.6 Å), naphthol yellow S (8.0 Å), 8-hydroxy-7-iodo-5-quinolinesulfonic acid (7.0 Å), so-

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(12) The nanoporous polymer (β-CD-HDI) has a composition of $C_{102}H_{174}N_{15}O_{57}\cdot 7H_2O$. Anal. Found for $C_{102}H_{174}N_{15}O_{57}\cdot 7H_2O$: C, 48.11; H, 7.11; N, 8.76. Calcd: C, 48.57; H, 6.90; N, 8.33. The presence of 5% H_2O was also confirmed by DSC measurements.

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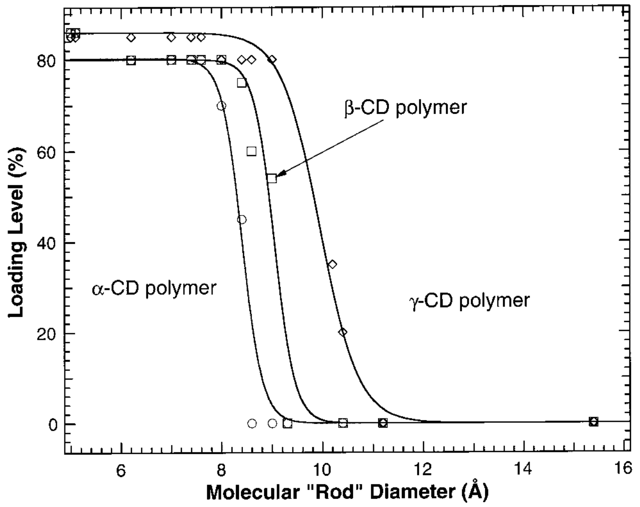

Figure 1. Pore size and its distribution of α-cyclodextrin-HDI (circles), β-cyclodextrin-HDI (squares), and γ-cyclodextrin-HDI (diamonds) polymers based on solute rejection measurements (see the text), which show a sharp rejection characteristic indicating narrow pore size distribution in the nanometer region (7−11 Å).

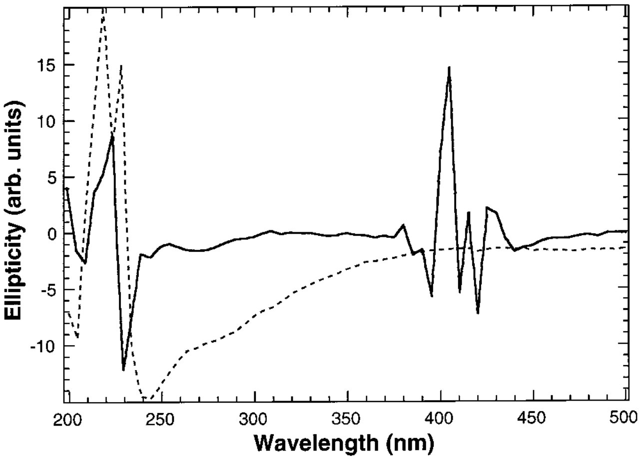

Figure 2. Circular dichroic spectra for (a) *p*-nitrophenol spontaneously intercalating into an optical-quality free-standing β-CD-HDI (solid line) film and (b) the same β-CD-HDI film without *p*-nitrophenol guests (dashed line).

dium 6-hydroxyl-2-naphthalenesulfonate (7.6 Å), and 8-hydroxy-7-(4-sulfo-1-naphthylazo)-5-quinolinesulfonic acid, disodium salt (8.4 Å). For β-cyclodextrin polymers, molecules with larger diameters such as (*R*)-(−)-*N*-(3,5)-dinitrobenzoyl-α-phenylglycine (8.6 Å) and 1,3,6,8-pyrenetetrasulfonic acid tetrasodium salt (9.0 Å) are also included in addition to all the compounds included by α-cyclodextrin polymers. As expected, γ-cyclodextrin polymers are able to include molecules with a rod diameter up to 10.5 Å. Examples of such molecules are brilliant blue (9.4 Å) and arsenazo III (10.4 Å), which fail to incorporate into α- and β-cyclodextrin polymers. Furthermore, molecules with bulky structures fail to intercalate into all cyclodextrin polymers. Examples of these molecules include trypan blue (11.0 Å), ponceau S (11.2 Å), and nickel phthalocyaninetetrasulfonic acid, tertrasodium salt (15.4 Å). These results confirm the nanoporosity of 7−8.5 Å for α-cyclodextrin polymers, 8−9 Å for β-cyclodextrin polymers, and 9−10.5 Å for γ-cyclodextrin polymers (Figure 1). In any case, the polymers have no pore larger than 25 Å according to BET measurements.

A key point is how organic guest molecules are incorporated from aqueous solution into these solid nanoporous polymeric materials. Are they located in the space inside or outside of cyclodextrins? To address this issue, we have turned to circular dichroism.

To have a circular dichroic absorption, the compound must possess both chirality and electron−optical absorption.[13,14] Chiral cyclodextrin does not absorb light and most guest molecules (such as *p*-nitrophenol) absorb light, but they are not chiral. An *induced* circular dichroism will be observed *only* when the cyclodextrin and the guest compound form a new complex that possess both chirality and optical absorption. Figure 2 shows the circular dichroic spectra for β-cyclodextrin-HDI polymer with *p*-nitrophenol intercalation from an aqueous solution; an induced circular dichroic signal with fine structures was observed at 405 nm. In solution, most cyclodextrin inclusion complexes have a single positive circular dichroic absorption, indicating that polar nitrophenols are *loosely* inside and parallel along the cyclodextrin cylindrical cavities. On the contrary, negative circular dichroic absorptions would suggest that the nitrophenols were perpendicular to the cyclodextrin cylindrical cavities.[15-17] However, the following factors cause a Cotton effect or the splitting of the circular dichroism absorption. First, occurrence of stacking introduces dipole−dipole interactions between the electric transition moment of intramolecular charge transfer within nitrophenol ($\lambda_{\max} = 405$ nm). The resulting Cotton effects tend to be positive when the angle between the transition moments is greater than 90°.[18] Second, long substitutions on the cyclodextrin torus, which extend the cyclodextrin nanochannels, seem to yield positive Cotton effects because of a *tight* fit between guest and host.[18] These results are consistent with the highly cross-linked, three-dimensional structures interconnected with cyclodextrin nanochannels filled with guest molecules. It further indicates that guest molecules are transported from an aqueous solution into the solid of the polymer through these channels, yielding a positive fine Cotton effect at 405 nm, as shown in Figure 2.

Noncovalent attractions are remarkably strong between nanoporous polymers and guest molecules, which is manifested from the formation constant *K* of inclusion complexes summarized in Table 1.[19] These observed inclusion formation constants, $K = 10^8 - 10^9$ M^{-1}, are

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Table 1. Observed Inclusion Formation Constants K^a for Various Cyclodextrin Polymers at Low Loading of Organic Guests at Room Temperature

cyclodextrin polymers[b]	organic guest molecules	formation constant, K (M^{-1})	loading level[c] (mg/cm^3)	ΔG (kcal/mol)
β-CD-HDI	*p*-nitrophenol	5×10^9	40 (86%)	−13.2
β-CD-TDI	*p*-nitrophenol	2×10^9	37 (78%)	−12.7
β-CD-HDI	toluene	3×10^7	≥18 (60%)	−10.2
β-CD-OMe-HDI	toluene	1×10^8	≥17 (56%)	−10.9
β-CD-HDI	trichloroethylene	1.8×10^8	≥38 (87%)	−11.2
β-CD-OMe-HDI	trichloroethylene	2.2×10^9	≥35 (79%)	−12.7

[a] See ref 19. [b] β-CD-HDI, polymer from β-cyclodextrin (CD) and hexamethylene diisocyanate (HDI); β-CD-TDI, polymer from β-cyclodextrin (CD) and toluene 2,6-diisocyanate (TDI); β-CD-OMe-HDI, polymer from partially methylated β-cyclodextrin (CD) and hexamethylene diisocyanate (HDI). [c] Data in parentheses correspond to the percentage of organics to cyclodextrin units in the polymer.

among the largest formation constants for noncovalent inclusion phenomenon. Thermodynamically, this process of guest molecules intercalating into nanoporous polymers is “downhill” or spontaneous with a driving force of $\Delta G°(298K) = -10$ to -13 kcal/mol ($\Delta G° = -RT \ln K$). At saturation, the nanoporous polymers have a capacity up to 20−40 mg organics/cm^3 of the polymer, which is the maximum loading levels listed in Table 1.

For most chemical reactions, the reaction is considered irreversible if the formation constant is on the order of $K = 2.0 \times 10^9\ M^{-1}$. However, host−guest interactions are noncovalent in nature and are highly dependent on the solvent used in the reaction. Therefore, the same inclusion reaction that seems irreversible in water is completely reversible in organic solvents such as ethanol. This is because organic guest molecules are hydrophobic; as a result, they are in a high-energy state *in water* and are strongly forced into the polymeric cyclodextrin cavities. In organic solvents at room temperature, the binding between polymeric cyclodextrins and organic guest molecules is rather weak ($K_{EtOH} \approx 21\ M^{-1}$; $\Delta G \approx 1.8$ kcal/mol). The polymeric cyclodextrin releases its organic “guest” with zero-order kinetics ($v = k_{-1}S$; $k_{-1} = 1.4 \times 10^{-5}\ M\ h^{-1}\ m^{-2}$) when the host polymer is exposed to ethanol. The reverse inclusion in ethanol has a low activation energy ($E_a \sim 15$ kcal/mol) and its kinetic rate increases rapidly with temperature.

To summarize, we have discussed two inclusion processes at liquid−solid interfaces that are thermodynamically favorable: (1) organic guests entering nanoporous polymers in water ($\Delta G < 0$) and (2) organic guests departing nanoporous polymers in ethanol ($\Delta G \sim 0$). The process of inclusion organic guests inside cyclodextrin polymers at water−solid interfaces seem to be driven dual-fold: (1) optimization of van der Waals or hydrophobic interactions between host cavities and guest molecules and (2) the release of guest molecules which leads to the formation of more hydrogen bonds in water. Another conclusion is that the formation constant (K) depends strongly on the solvent. In aqueous solvent, the formation of inclusion complexes is strongly favored; whereas, the inclusion reaction is completely reversible in organic solvent. Because of its reversibility, the polymers can be regenerated and recycled, thereby dramatically improving cost-effectiveness. We expect that these nanoporous polymers will have a great potential for water purification because they exhibit remarkable binding affinity to *inert* small organic guest molecules in water.

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