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Structure-Scavenging Abilities of Cyclodextrin-Based Polyurethanes

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Abstract

Cyclodextrins are ring-shaped molecules containing an apolar cavity with a diameter 4–8 Å wide and approximately 8 Å deep. Because of the hydrophilic nature of the surface, the materials are readily dispersed in water. However, hydrophobic groups on the inner surface of the nanoporous molecules attract hydrophobic organics that bind noncovalently to the apolar cavity. Recently, polycyclodextrins have been developed as binders for energetic materials and as sorbants for biological materials, and exhibit potential for development as sorbant materials for water filtration. Studies using these polymers have been reported in the literature and show that the polycyclodextrins are very effective scavengers of organic contaminants in water. Our work expands on the use of cyclodextrins in polymers through the synthesis of several organic cyclodextrin-based polymers. These filtering materials have been shown to scavenge several different kinds of contaminants up to parts per million concentrations from water. Some neutron work has been done to try to ascertain the nature of capture of these contaminants.

Acknowledgments

The authors would also like to acknowledge financial support from the U.S. Army Research Laboratory (ARL) Director's Research Initiative (DRI) Program. The authors would like to acknowledge the use of the facilities at the National Institute of Standards and Technology (NIST) Center for Neutron Research in performing all of the 30-m small angle neutron scattering experiments.

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1. Introduction

Since their discovery in 1891 by Villiers, cyclodextrins (CDs) have been the subject of increasing scientific study. The concentrated focus on CDs is due to a combination of their interesting properties and structure. As their name implies, CDs are ring-shaped molecules composed of D(+)-glucopyranose units linked through α-(1, 4) glycosidic bonds. Cyclodextrins are designated α-, β-, or γ-, denoting the number of glucose units as 6, 7, or 8, respectively (Figure 1). Cyclodextrins are produced by the enzymatic degradation of starch. The resulting product is a mixture of α-, β-, and γ-cyclodextrins, smaller amounts of higher analogs, and linear oligosaccharides. Purification is carried out through selective precipitation in appropriate solvents [1].

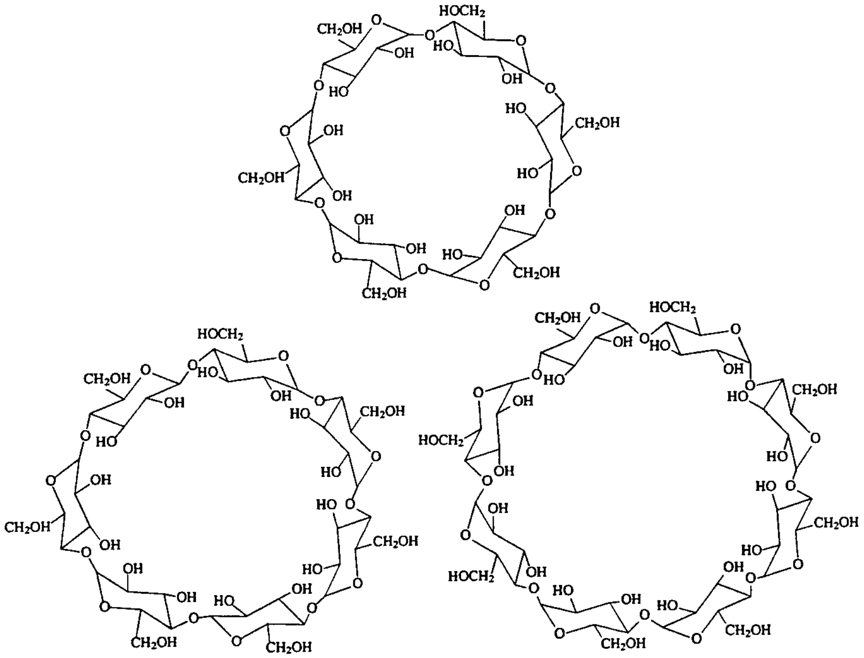

Figure 1. Chemical structure of α (6), β (7), and γ (8) cyclodextrin molecules.

The conformation of the CD ring structure is such that the secondary hydroxyl groups, on carbons two and three, are confined to one side of the ring, while the primary hydroxyl group on carbon six is restricted to the other side of the ring (Figure 2). The glucose rings are slightly tilted from the axis of the ring, with the primary hydroxyl groups angled inward. This gives CDs a hollow, truncated cone structure (Figure 3). The size of the CD ring increases with the number

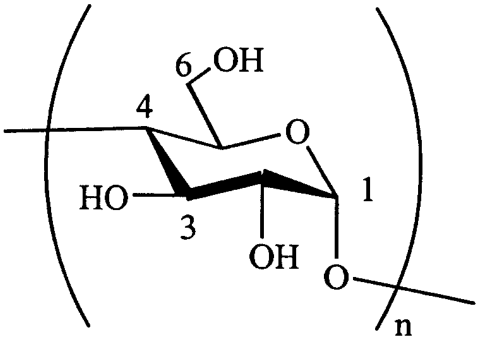

Figure 2. Chemical structure and carbon labeling of one glucopyranose unit.

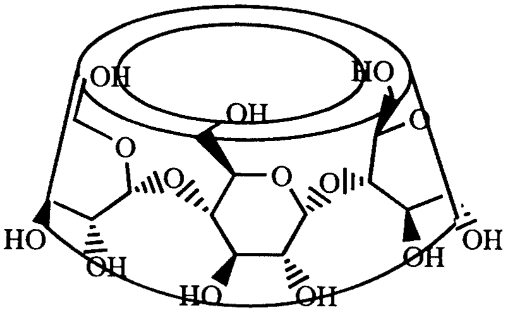

Figure 3. Truncated cone structure of cyclodextrins.

of glucose units, the interior minimum diameter for α, β, and γ, cyclodextrins being 4.9, 6.2, and 7.9 Å, respectively. The depth of the cavity is constant at 7.9 Å.

The positioning of the hydroxyls about the CD gives the exterior a hydrophilic character, while the interior is generally apolar or hydrophobic. This fact makes CDs excellent candidates for the formation of host-guest complexes. The driving force for complex formation can arise from coulombic, dipole-dipole, van der Waals, solvatophobic, or hydrogen bonding interactions between the host and the guest [2, 3]. These interactions are dependent upon specific molecular arrangement of the host and guest. In the case of CD complexes, this generally means that at least some part of a hydrophobic guest molecule must fit within the CD cavity (Figure 4). Long, thin guests may thread through the CD cavity, while more bulky molecules may only partially reside within the cavity. Complexes in which the guest molecule is held within the host molecule are termed "inclusion compounds," as opposed to association compounds, where the guest lies outside the cavity. However, reversing the complexation and removing the contaminants from the CD complex can be accomplished by washing the materials with an alcohol.

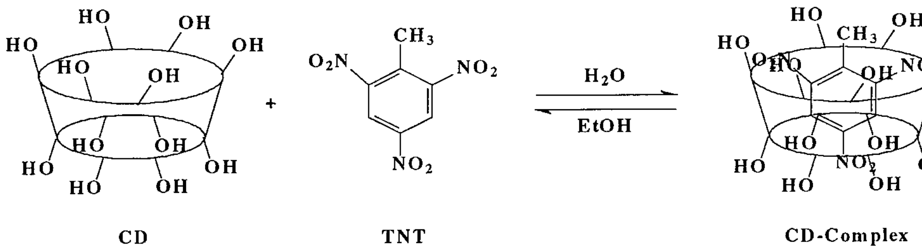

Figure 4. Host-guest complexation in cyclodextrin materials.

There are a great number of species that form inclusion complexes with CDs. The complexes are usually formed in water, with guests that are marginally soluble. Through the formation of a complex, a guest molecule will experience a more energetically favorable environment. The hydrophobic moieties of the guests prefer to interact with the hydrophobic CDs cavity rather than the solvent, while the outer surface of the CDs interacts with the solvent [4]. CDs have also been shown to selectively form complexes with one component of a racemic mixture [5].

Because CDs are natural products produced from a renewable resource and are generally non-toxic, much of the research involving CDs is concerned with the formation of complexes and their applications many specifically related to pharmaceuticals and food processing applications [2, 4, 6, 7]. Improved solubility of guest molecules brings significant benefits to drug delivery systems, where the active compound may not be soluble in an aqueous solution. CDs have been used in the food industry to mask unwanted odors, remove fats, and stabilize flavor [3]. In addition to their ability to form useful complexes, CDs are of interest for industrial applications. The most viable application for the unique host-guest chemistry of the CD molecules lies within the prospect of using the cyclodextrins to remove organic contaminants from water.

Polyurethane polymer synthesis incorporating CD molecules was reported in the early 1980s by Shono and coworkers [8–10]. Polyurethane polymers incorporating CDs were made from phenylene diisocyanate (PDI) and 2,4-toluene diisocyanate (TDI). These polymers were then used in chromatography columns for separations of solvents with similar boiling points and in the separation of aromatic amino acids. In both cases, the polymer was able to separate the solvents and small molecules very efficiently.

More recently, polyurethane materials incorporating CD molecules made from 1,6-diisocyanatohexane (HDI) and TDI gained more attention when Li and coworkers reported the synthesis of "new, novel" nanoporous polymers [11–13].

In these polymers, no other glycol unit was used in the polymer, the cyclodextrin:diisocyanate ratio was 1:8, and the polymerizations were done in dimethylformamide (DMF) at about 70 °C. This work investigated the capabilities of the CD-polymers to scavenge contaminants such as 4-nitrophenol, toluene, and trichloroethylene (contaminants found in drinking water in many places) from water. Li's work specifically investigated formation constants, κ, for the inclusion complexes. He discovered that the affinities of the contaminants for the CDs within the polymer were some of the highest ever observed (10^8–0^9 M^{-1}) for noncovalent inclusion phenomena. These researchers theorized from their work that while the CD-polymers have a low surface area, they could be loaded to a similar extent as activated carbon. The work also revealed that the process was a completely reversible process when hydrophobic organic guest molecules, such as an alcohol, are used to rinse the material.

Mach I* recently reported synthesis of a variety of CD-based polymers, including poly(1-chloro-2,3-epoxy propane)-CD and poly(methylene bis[phenyl isocyanate])(MDI)-CD [14–15]. The purpose of their small business innovative research (SBIR) work was to develop materials with explosive that would render them less shock sensitive. The cyclodextrin materials did show that they could be used to encapsulate energetic materials such as cyclotrimethylenetrinitramine (RDX) and that the materials were less shock sensitive.

In addition, Mach I, Ito and coworkers [16], and Geckeler and coworkers [17] looked into the development of CD nanotubes structures. It has been suggested that these materials, because of the short spacer groups used to chain them together, form well-ordered, nanotube-like structures. In Ito's work, the CDs were molecularly strung onto polyethylene glycol (PEG). In order to prevent unstringing of the inclusion complex of the PEG and CDs, bulky groups were often covalently attached to the chain ends. Geckeler and coworkers used CDs molecularly strung onto the backbone of the polymer chain in order to increase solubility of the polymer. None of the research groups verified the well-ordered structure through traditional structural techniques, such as small-angle x-ray or neutron scattering.

The goal of this project was to synthesize a series of structurally unique CD-based polyurethane polymers and to then determine the ability of these polymers to form host-guest associations based on noncovalent binding of organic contaminant molecules. Traditional chemical analyses, such as Fourier transform infrared (FTIR), nuclear magnetic resonance (NMR), and thermal gravimetric analysis (TGA), were used to characterize the polymers. Testing of polymer properties was done by determining the abilities of these polymers to scavenge in contaminant solutions of trinitrotoluene (TNT), RDX, and dimethylmethylphosphonate (DMMP) and by subsequently testing the

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* Mach I Chemicals, 340 East Church Road, King of Prussia, PA 19406.

"renewability" of the polymers, or how well the polymers can release the sorbed contaminant.

2. Experimental

2.1 Materials

β-CD was purchased from Wacker Biochem Corporation.* Tetrahydrofuran (THF), DMF, ethanol, methanol, and PDI were purchased from Aldrich Chemical Company.† Methyl chloride, hexanes, ethylene glycol, polyethylene glycol (MW=200, ~3.5 repeat units), ethyl acetate, toluene, MDI, TDI, and HDI were purchased from VWR Scientific.‡ All materials were used as received unless otherwise noted. All water used was high-performance liquid chromatography (HPLC) grade unless otherwise noted.

2.2 Reference Polyurethane Material Synthesis

Synthesis of polyurethanes occurs in very straightforward reactions, which involve a substitution nucleophilic bimolecular (SN2) reaction between a diol and a diisocyanate (Figure 5). Synthesis was performed using polyethylene glycol and four different isocyanates (PDI, HDI, MDI, and TDI) as shown in Figure 6. While all of these polyurethane materials have previously been synthesized by other researchers, it will be useful to have some data to compare with our new contaminant scavenging studies [8–18]. Initially, a closed atmosphere three-necked reaction flask kept under nitrogen purge was used to house the reaction. This method was substituted with a much simpler mixing of the chemicals in a beaker and covered with a watch glass. The atmospheric purge was not necessary in polyurethane synthesis and by using the three-necked flask, it was much too difficult to remove the product after the synthesis was complete. Monomers were added to the beaker and stirred while heating (70 °C). Had a catalyst been used, heating might not have been necessary. However, since a catalyst could get trapped within the polymer chains and contaminate the polymer, no catalyst was used with the experiments. Some of the isocyanates (PDI, MDI) were solid; therefore, they required higher temperatures, above the melting temperature of the monomer, in the flask in order to have good mixing between the diol and diisocyanate.

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[*] Wacker Biochem Corporation, 3301 Sutton Road, Adrian, MI 49221.

[†] Aldrich Chemical Company, P.O. Box 2060, Milwaukee, WI 53201.

[‡] VWR Scientific Products, 405 Heron Drive, P.O. Box 626, Bridgeport, NJ 08014.

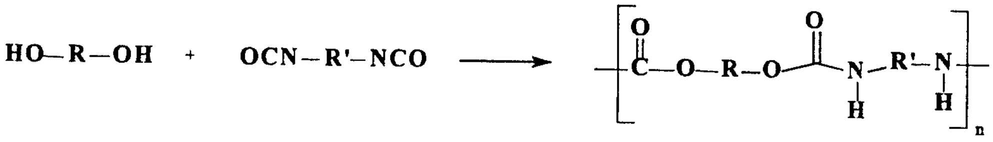
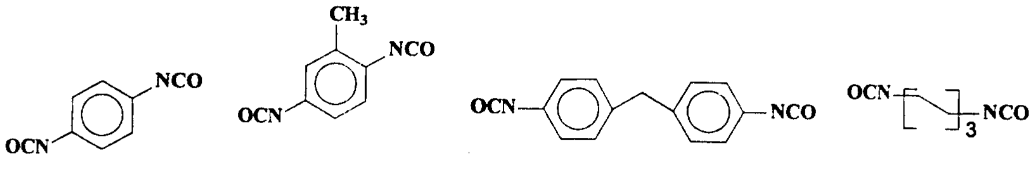


Figure 5. A general polyurethane synthesis reaction scheme.



PDI TDI MDI HDI

Figure 6. Isocyanate monomers (R') used in polyurethane synthesis.

2.3 CD-Based Polyurethane Material Synthesis

Two different CD-based polyurethane polymers were synthesized similarly to the reference polymers.

2.3.1 Diisocyanate:PEG:CD Materials

For these materials, some CD was substituted for polyethylene glycol. Again, while all of these polyurethane-CD materials have previously been synthesized by other researchers [8–18], it will be useful to have some data to compare with our new contaminant scavenging studies. Three separate CD-based polyurethanes were synthesized with each isocyanate, containing different amounts of CD: a polyurethane with 3-weight-percent CD, one with 11-weight-percent CD, and one with 40-weight-percent CD. The CD was dissolved in DMF, mixed with the other monomers in a 8:1.005:1.005 mole ratio between isocyanate:PEG:CD, respectively, leaving an excess of hydroxyl groups, and heated in order for the reaction to occur.

2.3.2 Diisocyanate:CD Materials

Synthesis was performed using only MDI and CD without the PEG chain extender. Four polymers containing different mole ratios of diisocyanate and CD were synthesized (6:1—36-weight-percent CD, 4:1—53-weight-percent CD, 3:1—60-weight-percent CD, and 1:1—82-weight-percent CD). These polymers were evaluated with respect to their varying CD content and also enabled a comparison between the scavenging properties of MDI-PEG-CD vs. the MDI-CD polymers.

2.4 Solubility

Solubility was tested on the pure CD material and on all of the polymers (reference and 3-weight-percent, 11-weight-percent, and 40-weight-percent) in

13 common solvents (Table 1). Typical solvent groups were used including polar organic solvents, halogenated solvents, and non-polar hydrocarbon solvents. These included: DMF, THF, ethanol, methanol, hexanes, ether, methyl chloride, ethyl acetate, chloroform, toluene, acetone, and water. Approximately 0.5 g of polymer was weighed out, added to 20 mL of solution, and allowed to set for 24 hr.

Table 1. Solubility testing results for CD monomer and CD-based polymers.

Solvent	Material				
	Pure CD	PDI-PEG With CD	TDI-PEG With CD	MDI-PEG With CD	HDI-PEG With CD
Water	Soluble	Insoluble	Insoluble	Insoluble	Insoluble
Methanol	Slightly Soluble	Insoluble	Insoluble	Insoluble	Insoluble
Ethanol	Slightly Soluble	Insoluble	Insoluble	Insoluble	Insoluble
THF	Slightly Soluble	Insoluble	Insoluble[a]	Insoluble	Insoluble
DMF	Soluble	Insoluble	Insoluble[a]	Insoluble	Insoluble
DMSO	Soluble	Insoluble	Insoluble	Insoluble	Insoluble
Ethyl Acetate	Slightly Soluble	Insoluble	Insoluble	Insoluble	Insoluble
Acetone	Slightly Soluble	Insoluble	Insoluble[a]	Insoluble	Insoluble[a]
Ether	Slightly Soluble	Insoluble	Insoluble	Insoluble	Insoluble[a]
Toluene	Slightly Soluble	Insoluble	Insoluble	Insoluble	Insoluble
Hexanes	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble
Methylene Chloride	Insoluble	Insoluble	Insoluble[a]	Insoluble	Insoluble
Chloroform	Insoluble	Insoluble	Insoluble[a]	Insoluble	Insoluble[a]

[a] Standard polymer (polymer without CD) was completely or slightly soluble (swellable) in the listed solubility solvent.

2.5 FTIR Spectroscopy

Spectra were obtained using a Perkin Elmer Spectrum 2000 FTIR spectrometer. Data was collected in a spectral range of 379–4000 cm^{-1}. The number of sample scans and resolution were 128 and 4 cm^{-1}, respectively. FTIR spectroscopy yields structural information and is used to verify the presence of specific molecules. Several references were used to assign details for spectra [19–21].

2.6 ^{13}C Solid State NMR Spectroscopy

^{13}C NMR spectra were obtained on a Varian Inova 200 spectrometer operating at a frequency of 50 MHz for the ^{13}C nucleus. A Doty Scientific 7-mm High-Speed CP/MAS probe was used. Ground samples were packed in 7-mm fused zirconia rotors (thick walled) and sealed with Kel-FTM caps. Sample spinning rate was ~3 kHz. Magic angle spinning with high-power decoupling was utilized. The number of scans acquired per sample varied but were at minimum 1000 for long recycle delays, depending on desired signal:noise. All chemical shifts were referenced to TMS. All NMR spectra were evaluated utilizing the GRAMS/32 AI Spectral Notebase software version 6.00. NMR spectra yield quantitative structural information and are used to determine the precise structure of the monomers and/or polymers.

2.7 TGA

Experiments were conducted using a TA Instruments TGA 2950 Thermogravimetric Analyzer. Single scan runs were performed from 20° to 800 °C at 20 °C/min. Degradation temperatures, T_d, are reported as the onset of thermal degradation which are calculated using the second derivative plot of the TA Instruments Universal Analysis Software. Sample sizes varied between 10 and 20 mg.

2.8 DSC

DSC measurements were carried out on 3- to 10-mg samples with a TA Instruments thermal analyzer equipped with a liquid nitrogen cooling system. A heating rate of 10 °C/min was employed, and an indium standard was used for calibration.

2.9 Small-Angle Neutron Scattering (SANS)

SANS measurements were performed at the National Institute of Standards and Technology (NIST) Center for Neutron Research in Gaithersburg, MD, using the 30-m SANS spectrometer located at NG-7.

SANS samples included: (1) TNT-H_2O solution, (2) CD powder, (3) CD dissolved in water, (4) CD in TNT-H_2O solution, (5) poly-PDI-PEG-CD-41 dry, (6) solid poly-CD in TNT-H_2O solution, and (7) poly-PDI reference. No special precautions were taken with the samples (no drying of sample prior to analysis); all samples were prepared in a room at 22 °C and 55% relative humidity. Samples were enclosed in 1-mm path length quartz cells and maintained at 25.0 ± 0.2 °C. The samples were typically made 24 hr prior to SANS measurements.

The scattering intensity was measured as a function of q, the magnitude of the scattering vector. q is related to the scattering angle, θ, by the relationship

$q = \frac{4\pi}{\lambda}\sin\left(\frac{\theta}{2}\right)$, where λ is the wavelength of the incident neutron beam ($\lambda = 6$ Å for these experiments). The detector was a 64 × 64 cm^2 He-3 position-sensitive proportional counter with 1-cm^2 resolution. Scattered intensity was measured at q values ranging from ~0.002 Å^{-1} to ~0.6 Å^{-1}. This was accomplished by placing the detector at various distances from the sample. The positions of the circular pinholes before the sample were adjusted to match the resolution of the detector configuration. Data were corrected for the scattering from an empty quartz sample cell, detector background and sensitivity, and the transmission value of each sample. Absolute scattering intensities were obtained by reduction of the raw data through calibration with the measured incident neutron intensity.

2.10 Wide-Angle X-ray Diffraction (XRD)

X-ray scattering data was collected using a Bruker D5005 powder X-ray diffractometer. X-rays are generated using a tube source operated at 40 kV and 40 mA, with $\lambda = 1.54$ Å. Collimation and focusing are achieved with slits and a Gobel mirror.

2.11 High-Performance Liquid Chromatography (HPLC)

2.11.1 TNT and RDX Contaminant Samples

Reverse phase HPLC analysis was performed using a Hewlett Packard (HP) 1090 Series II liquid chromatograph equipped with diode array detector and Luna 5-µm C18 250 × 4.6-mm column held at 40 °C. Isocratic solvent compositions used for TNT analysis were 30% water and 70% methanol. For RDX analysis, 50% water and 50% methanol were used. Ultraviolet (UV) signals were gathered at 230 nm, flow rate was set to 1 mL/min, and injection volume was 20 µL. The amounts of contaminant (TNT or RDX) were calculated on comparison of the area under the peak (measured at 230 nm, integrated manually) with a calibration curve obtained from injecting a solution with a known concentration of contaminant.

2.11.2 DMMP Contaminant Samples

An HP 5972 gas chromatograph/mass spectrometer (GC/MS) was used to analyze samples for DMMP concentration. Experimental conditions were as follows: Samples were scanned from 10–200 m/z, the injection port was set to 250 °C, the transfer line was set to 280 °C, the split was set to 20 mL, the solvent delay was 4 min, injection volume was 2 µL and oven temperature programming was 50–150 °C at 10 °C/min. The carrier gas was helium and was set at ~1 mL/min. Amounts of contaminant (DMMP) were calculated on comparison with a calibration curve obtained from solutions of DMMP with known concentration.

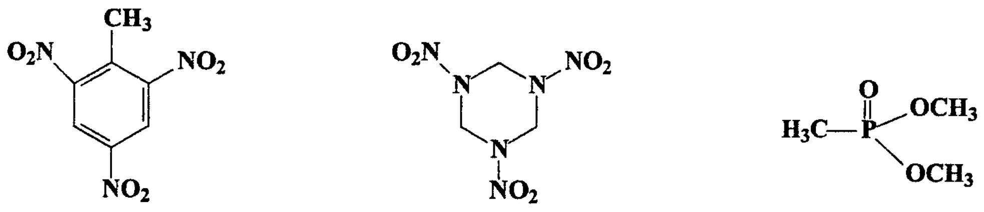
Amount of DMMP in samples was determined based on the area of the peak comprised from the sum of all atomic units (au) between 61 and 126 m/z, with the baseline drawn at 100-au level.

2.12 Scavenging Studies

Stock solutions with known concentrations of TNT, RDX, and DMMP were prepared in water (Figure 7). When dissolving explosive contaminants, there are issues concerning solubility. These solubility difficulties lead to different standard concentrations in the three stock solutions (TNT—19.4 ppm, RDX—13.04 ppm, and DMMP—20.9 ppm). Four polymers (PDI-PEG-CD-41-weight-percent, HDI-PEG-CD-40-weight-percent, MDI-PEG-CD-32-weight-percent, and TDI-PEG-CD-40-weight-percent) were individually tested for scavenging ability in each of the stock contaminant solutions. Prior to performing the scavenging studies, the polymers were purified to remove any excess reactants or possible contaminants. The polymers were allowed to set in water for four days before being filtered and soaked in ethanol for 3 hr. The polymers were then allowed to dry overnight. Fifty milliliters of the stock contaminant solution and 0.5 g of polymer was added to a 150-mL beaker. The polymer-charged solution was then stirred for 3 hr. The polymer-contaminant solution was then filtered, and the filtrate was analyzed using HPLC to determine the amount of remaining contaminant in the water. To determine the ability of the complexed polymers to release contaminant molecules, the complexed polymers were placed in ethanol (exact amount varies) and stirred for 1 hr. The polymers were then filtered from the ethanol solution, and the ethanol filtrate was analyzed using HPLC. The HPLC analysis provides a quantitative evaluation of how much contaminant the CD polymers can scavenge from solutions and the degree that the complexation with the polymers can be reversed by rinsing in alcohol. In separate evaluations, an 18-hr test and a 44-hr test were performed with TNT to determine whether increased exposure to the contaminant would increase the scavenging uptake of the CD. The ethanol wash served to determine the degree of renewability the polymers possessed. By analyzing the ethanol used to rinse the polymers, the degree to which these polymers can release their captured contaminants and create space for new contaminants could be assessed.

2.13 UV/Visible Spectroscopy (UV/Vis)

UV/Vis measurements were conducted with a dispersive UV-Vis-NIR spectrophotometer, possessing a R928 photomultiplier tube. Samples were put into Sabia liquid cells, which absorb in the 2100- to 2500-nm range (not interfering with the sample absorbance). Samples were scanned between 190 and 750 nm at a scan rate of 200 nm/min. Only TNT samples were run to compare the UV/Vis method with the HPLC method.



TNT **RDX** **DMMP**

Figure 7. Chemical structure of contaminants used in scavenging studies.

3. Results and Discussion

Initially, polymer synthesis for PDI and TDI polymers was performed identically to that used by Li and coworkers, using a CD:diisocyanate ratio of 1:8 [12, 13]. These polymers, however, showed no solubility in any of the variety of solvents planned for the solubility studies. It is common in polyurethane synthesis to use a diol molecule as a spacer unit. As the length of the spacer unit increases, often so does the solubility of the polymer material. Polyethylene glycol was chosen as an initial candidate as a spacer unit because it is cheap, readily available, and can be obtained in many different molecular weights. The results for the solubility studies for the polymer materials using polyethylene glycol are shown in Table 1. The use of polyethylene glycol did not appear to help the solubility of the polymeric materials, as all polyurethane-CD materials are insoluble. A discussion of possible reasons for the lack of solubility will be given later in this report. Some of the polymer standards, those made without cyclodextrin, had limited solubility in the range of solvents for the solubility tests but they are not listed here due to space constraints. The polyurethane-CD materials noted with a superscript "a" indicate that the standard polymer (the polymer without CD) was completely or slightly soluble (swellable) in the listed solubility solvent.

3.1 FTIR Studies

For all four polyurethane-CD materials synthesized in the current experiments, the FTIR spectrum for the polymer has some notable differences from the spectra of their reactants. Since all four polyurethane-CD materials have similar changes, a general discussion will be included rather than discussion of each individual set of spectra. The FTIR series for poly(PDI-PEG-CD-41-weight-percent) is shown in Figure 8, the poly(TDI-PEG-CD-40-weight-percent) series is shown in Figure 9, the poly(MDI-PEG-CD-32-weight-percent) series is shown in Figure 10, and the poly(HDI-PEG-CD-41-weight-percent) series is shown in Figure 11. The spectra in the figures are offset in order to observe details of the materials, and the spectra indicate that the synthesis was successful. The

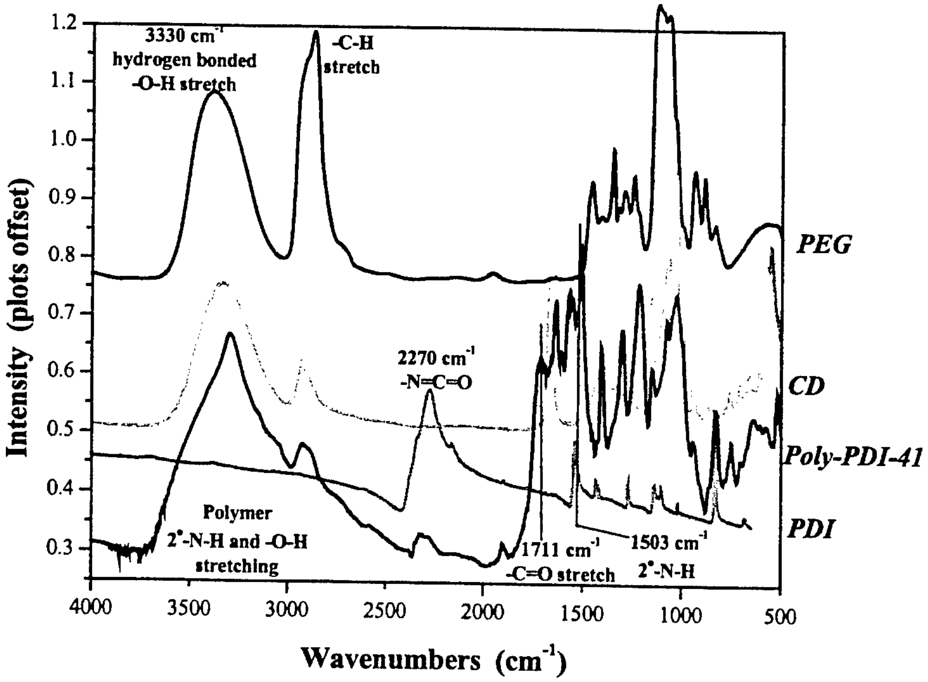


Figure 8. FTIR series for poly(PDI-PEG-CD-41-weight-percent).

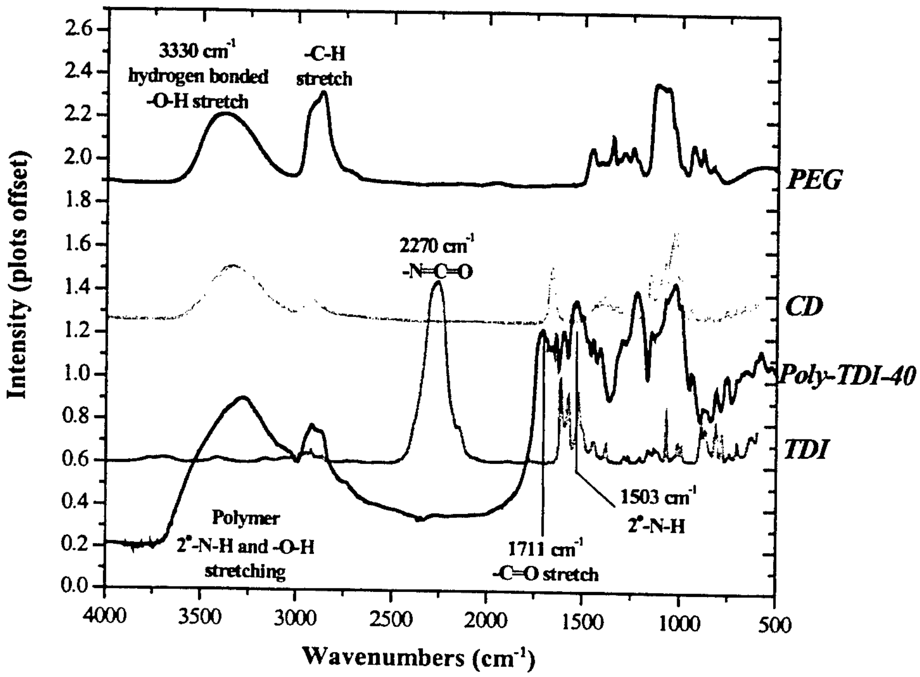


Figure 9. FTIR series for poly(TDI-PEG-CD-40-weight-percent).

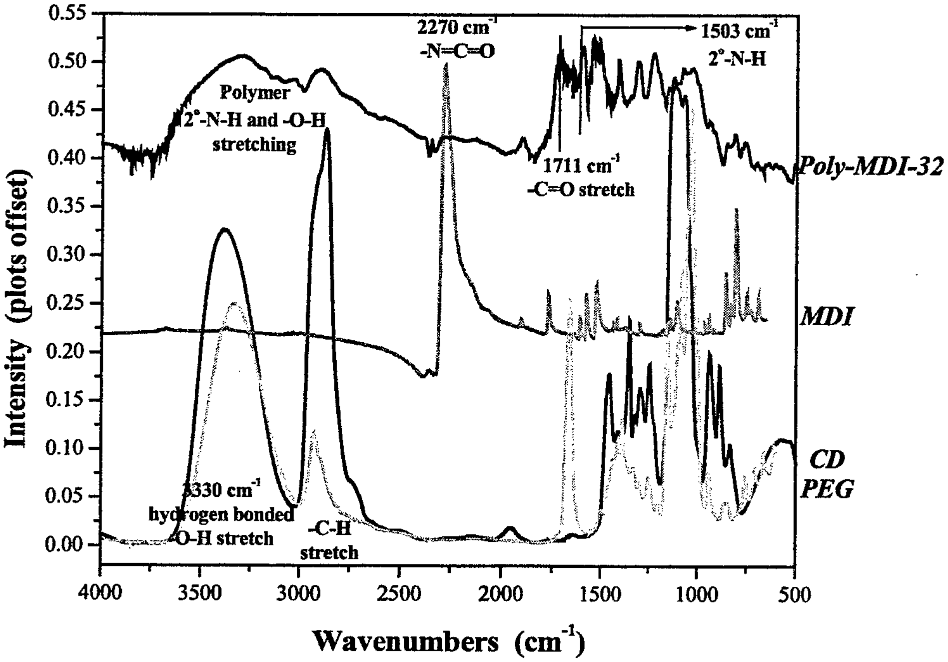


Figure 10. FTIR series for poly(MDI-PEG-CD-32-weight-percent).

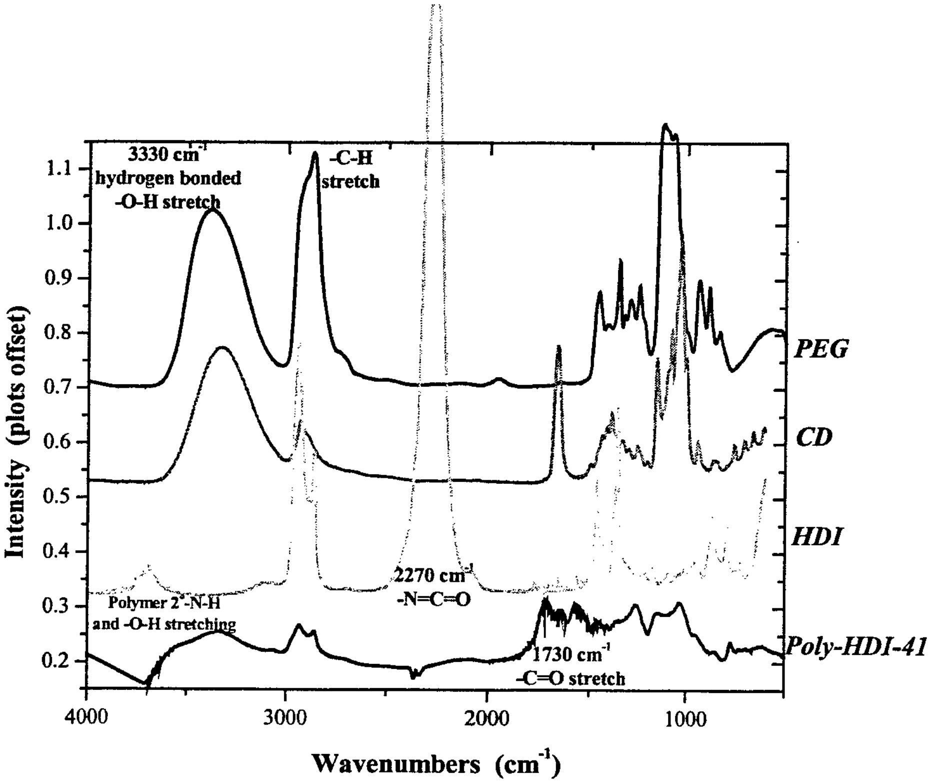


Figure 11. FTIR series for poly(HDI-PEG-CD-41-weight-percent).

disappearance of the isocyanate peak (2270 cm^{-1}) indicates that all the isocyanate groups were used in the reaction. The appearance of amide C=O (1711 cm^{-1}), N-H band of a secondary amide (1503 cm^{-1}) (amide II), and a C-N stretching band (1280 cm^{-1}) indicate that the polymer was formed. Typically, disappearance of the hydroxyl groups (3330 cm^{-1}) would also be observed and would indicate that the reaction went to completion but, in this case, the CD monomer has 21 hydroxyl groups per molecule but the isocyanate was the limiting reagent and not all hydroxyls were used in the reaction in an effort to keep crosslinking to a minimum. Therefore, the broad band at 3300-3500 cm^{-1} is indicative of both hydrogen bonded hydroxyl groups and secondary amide groups. Most of these features have previously been reported in the literature [13, 22].

3.2 NMR

NMR spectra were taken of the TDI-PEG polymer standard and TDI-PEG-CD-40-weight-percent polymer. Polymer spectra contain notoriously broad peaks that are difficult to extract quantitative data from. However, both spectra did contain peaks indicating various carbon groups including benzene rings, methyl and methylene groups, and methylene groups attached to hydroxyl groups. However, we were unable to resolve these peaks and therefore were unable to show distinction between the different sites of reactivity. Because the peaks were so broad and no useful data was extracted, the NMR spectra will not be shown here.

3.3 TGA

TGA was performed on the polymeric materials that were synthesized with and without CD. The onset temperatures of degradation (T_d) are shown in Table 2. T_d's for the polymers were measured using the TA Instruments Universal Analysis software. The peak maximum of the second derivative plot (of the primary weight loss transition) was used to determine T_d. The onset of thermal degradation of β-CD was measured at 371 °C. The T_d's measured for the polyurethanes (with 0% CD) ranged between 320° and 398 °C. Because the onset degradation of the polyurethanes is in the same general region as the β-CD, it is difficult to discern what chemical component of the CD-based polyurethane contributes to changes observed in thermal stability. The various polymers exhibit changes in T_d with regard to CD content, however, a general trend in T_d was not observed. Variability in the T_d values can be explained by the varying rates of thermal degradation (slope and breadth of the weight loss transition) for the different polymers as well as variations in post synthesis drying conditions.

Table 2. Degradation temperatures (T_d) for polyurethane and polyurethane-CD polymers.

Onset T_d (°C)					
Polymer	Weight-Percent CD in Polymer				
	0% CD	3% CD	11% CD	32% CD	40% CD
PDI-PEG	320	323	375	–	274
TDI-PEG	371	346	376	–	372
HDI-PEG	398	369	361	–	368
MDI-PEG	367	394	409	404	–

3.4 DSC

DSC was taken of PDI-PEG, PDI-PEG-CD 11%, and PDI-PEG-CD 41% samples. For all of the samples, no glass transition or crystallization temperatures were apparent, and the experiment was performed below sample degradation temperatures. A crystallization temperature was apparent in the pure CD thermogram. Incorporation of the CD into the polymer must repress the crystallinity of the CD molecules. Since no significant thermal trends were observed via DSC measurements, thermograms are not included in this report.

3.5 SANS

Many groups have previously hypothesized organization of the CD within the polymer chains [15, 16]. One hypothesis reported for CD research stated that CDs could pick up more contaminants in a polymer structure because the CD molecules would "line up" in the polymer chains, creating an ordering of the polymer [12, 13]. While this theory has never been proven, one of the best ways to study such ordering in polymer systems is through the use of small-angle scattering.

SANS plots were obtained for: (1) TNT-H_2O solution, (2) CD powder dry, (3) CD dissolved in water, (4) CD in TNT-H_2O solution, (5) poly-PDI-PEG-CD-41 dry, (6) solid poly-CD in TNT- H_2O solution, and (7) poly-PDI reference. The TNT-H_2O solution, CD powder dry, CD dissolved in water, CD in TNT-H_2O solution, and poly-PDI reference samples did not show any significant scattering features. The CD powder dry and poly-PDI reference samples can be seen in Figure 12. The poly-PDI-PEG-CD-41 dry sample does show Bragg scattering. Bragg scattering is an indication of ordering within a system. The Bragg peak observed in the cyclodextrin-polymer was fit with a Gaussian, which had an intensity value (m1) of -0.015236, a peak position (m2) of 0.085057, a standard deviation (m3) of -0.02668, and a correlation value (r) of 0.99411. From this fit, the d-spacing can be calculated from the peak position, or q value, using the

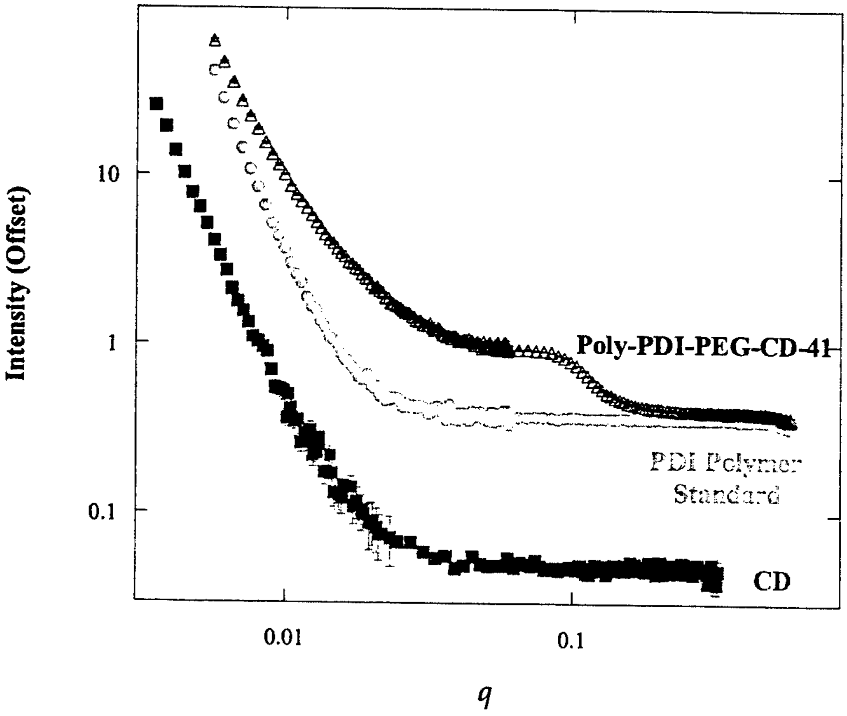


Figure 12. SANS plots of CD, PDI polymer standard, and PDI-PEG-CD polymer.

following equation: $q = \frac{4\pi}{\lambda}(\sin\theta) = \frac{2\pi}{d}$, where q is the peak position, λ is the wavelength mof the scattering, θ is the angle of the scattering, and d is the d-spacing. The d-spacing was found to be 73.87 Å (7.39 nm) or possibly about nine ordered cyclodextrin molecules. This is about double the length of a PEG unit.

The presence of Bragg spacing in the poly-PDI-PEG-CD-41 dry sample is significant. While ordering in these polymer systems had been hypothesized, it had never before been reported in any published reports. In addition, this long-range ordering is not present in the small molecule CD SANS plot or the poly-PDI reference sample SANS plot. This further indicates a significant degree of ordering of the poly-PDI-PEG-CD-41 dry sample over the other materials. What remains a mystery is how these systems could force such ordering since the materials are extremely crosslinked, rigid polymers. However, the scavenging/ renewability studies may be able to shed some light on this issue.

3.6 XRD

The idea of using XRD as a technique to study the cyclodextrin polymers was brought about because of the possible need to follow the trapping ability of the materials. Following the changes in crystallinity and crystal structure is one way to do this.

XRD was performed on CD and poly-PDI-PEG-CD-41 samples. CD monomer molecules exhibit a high degree of crystallinity and hydrogen bonding between samples. This is observed in Figure 13, containing plots of both the CD and poly-PDI-PEG-CD-41 samples. Here, it can be observed that when the CD is incorporated into a polymer system it completely disrupts the fine structure crystallinity of the CD materials. Only one peak is still observable at approximately 2θ = 18. By using the Bragg equation, a d-spacing of 2.49 Å can be calculated. This does not correspond to the diameter or depth (6.2 and 7.9 Å, respectively) of the β-CD and it is larger than a single C-C bond (1.54 Å). Apparently, some small-range crystalline ordering is occurring, and the ordering, evident from the broad peak, is polydisperse.

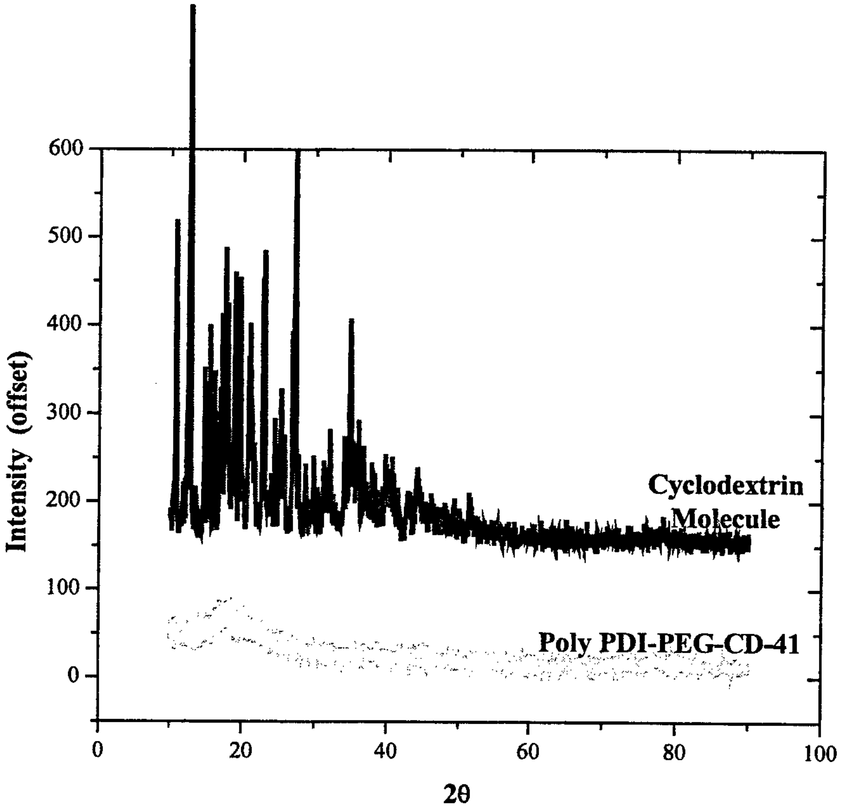


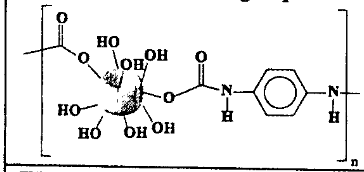
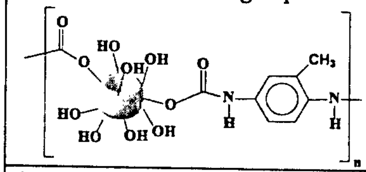
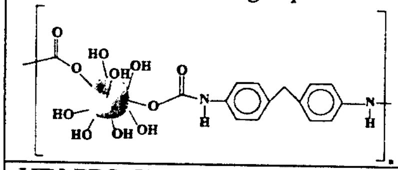
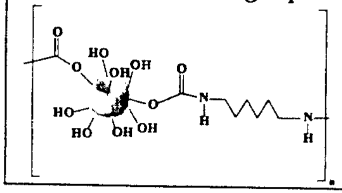
Figure 13. XRD plots of CD and poly PDI-PEG-CD-41.

3.7 HPLC/Contaminant Scavenging/Renewability Studies

All standard polymers (no cyclodextrin added) were treated, soaked in contaminant solutions and then tested for any "scavenging" capabilities. While no scavenging capabilities were expected, it is necessary to test the standard polymers to ensure that no other trapping factors are involved with the real results. Insignificant amounts of contaminant solution were absorbed by the non-CD polymers and, therefore, none of the data will be shown here.

Recall that all polyurethane-CD materials were soaked in TNT solutions for 3-, 18-, and 44-hr periods. See Table 3 for the resulting data from all of the contamination scavenging studies. The tabulated data shows the weight percent of contaminant absorbed from the dilute aqueous solutions.

Table 3. Percent contaminant absorbed from various contaminant solutions at various scavenging times.

Polymer Sample	Contaminant/Scavenging Time (hr)				
	TNT[a]/3	TNT[a]/18	TNT[a]/44	RDX[b]/3	DMMP[c]/3
PDI-PEG-CD 41-weight-percent 	48%	66%	69%	36%	21%
TDI-PEG-CD 40-weight-percent 	43%	65%	74%	30%	16%
MDI-PEG-CD 32-weight-percent 	8%	16%	29%	2%	4%
HDI-PEG-CD 41-weight-percent 	5%	10%	16%	2%	3%

[a] Starting contaminant concentration: 19.4 ppm.
[b] Starting contaminant concentration: 13.04 ppm.
[c] Starting contaminant concentration: 20.9 ppm.

In the 3-hr studies, HPLC revealed that the TNT concentration was nearly halved after exposure to two of the polyurethane-CD polymers with cyclodextrin additions (PDI-PEG-CD and TDI-PEG-CD), while the remaining two polymers (HDI-PEG-CD and MDI-PEG-CD) retrieved insignificant amounts of TNT. A preliminary examination of the tabulated data for the four polymer-contaminant solution systems revealed that the two polymers that proved to be effective in scavenging the contaminants were far better dispersed throughout the water. Originally, the theory was that the results may have been the result of finer grinding, as the two effective polymers were ground down to a powder leaving a greater surface area exposed to the contaminant solution, while the other two polymers consisted of slightly larger particles. However, both polymers were reground to a fine powder and still produced the same results. It is more likely that the molecular structure of the polymers played a significant role in the scavenging ability. An examination of the four structures of the polymers used in the scavenging study demonstrates that the two polymers (PDI-PEG-CD and TDI-PEG-CD) most effective at scavenging have very similar structures, whereas the two less effective polymers have very different structures (see Figure 6).

As might be expected, the 18- and 44-hr TNT studies reported increasingly better absorption for all polymers. The difference between 3- and 44-hr scavenging times is significant enough to suggest that the contaminants used in this study are not easily attracted to the hydrophobic cavity of the CD, at least when it is covalently bound to the polymer (Figure 14). With increased solution, the contaminant exposure in the molecules have more time to "find" the CDs in the polymer. However, then we might assume that in a little less than 2 days (44 hr) there would be plenty of time for all of the contaminants to be absorbed by the polyurethane-CD material and, that beyond this, it would be impractical for an actual membrane to be used for contaminant scavenging.

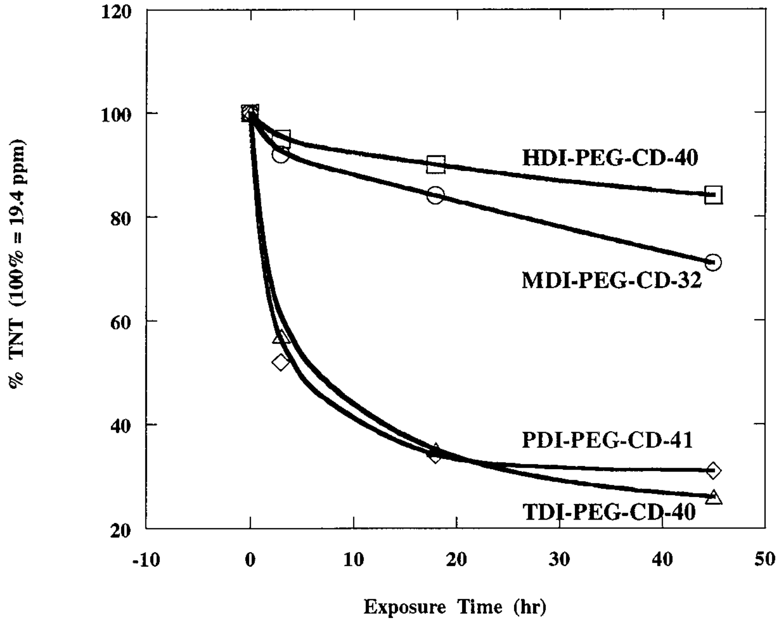


Figure 14. Correlation between different polymers and scavenging ability of TNT.

For these scavenging experiments, a significant excess of moles of CD to moles of contaminants (41:1) were used in each of the experiments, which should yield many opportunities for capture by CD molecules incorporated into the polyurethane. In addition, previous researchers have shown that CD polymers exhibit strong interactions with guest molecules, which contain π electrons and/or heteroatoms [9]. However, even in the 44-hr TNT solution exposure experiment there is still only 70–75% uptake of the contaminants from the solution for the PDI and TDI urethane polymers.

The 3-hr RDX and DMMP studies showed results similar to the TNT 3-hr study. The two similar polyurethane-CD structures (PDI-PEG-CD and TDI-PEG-CD) scavenged the RDX and DMMP solutions better than the two structures that were structurally unique in the experiment. In these experiments, the amount of contaminants scavenged from solution was significantly less than the 3-hr TNT studies. This is particularly surprising for RDX, which while not conjugated has a very similar chemical composition and structure. However, if recalling previous experiments by other researchers, guest molecules containing π electrons (conjugated systems) are much more likely to be absorbed by the CD molecules [9]. Therefore, it is reasonable that more TNT was absorbed as opposed to RDX or DMMP.

Table 4 shows the scavenging results for the MDI-CD polymers synthesized without the PEG chain extender. The data shows that the MDI-CD polymers exhibited much higher scavenging ability compared to the MDI-PEG-CD polymers. For these polymers, the RDX absorbed by the polymers increased with decreasing CD content. This suggests that CD content may not be as important as chemical structure for optimized scavenging ability. When the MDI-CD polymer containing approximately 36% CD is compared with the MDI-PEG-CD polymer (32% CD), the amount of RDX absorbed from solution increases from 2% (MDI-PEG-CD) to 64% (MDI-CD).

Table 4. MDI:CD scavenging studies with RDX.

Polymer	Weight-Percent CD	Mole Ratio (MDI:CD)	Weight-Percent RDX Scavenged From Water (20 hr)	Weight-Percent RDX Released by the Complexed Polymer Following Ethanol Wash
MDI-CD	82	1:1	19	29
MDI-CD	60	3:1	51	46
MDI-CD	53	4:1	61	78
MDI-CD	36	6:1	64	40

In order to gain a better understanding of the scavenging results, several possible explanations should be considered. Because of the high degree of crosslinking, the polymer chains will not have much free volume. How does this impact the ability of these polymers to scavenge contaminants from solution? The inability for the polymer chains to reorganize themselves through free volume effects or gyrations in the solution will restrict the contaminant molecule's ability to access all parts of the polymer chain. Therefore, one possibility is that the CDs were inaccessible to the contaminants, resulting in their inability to scavenge many molecules from solution.

Because of similarities, it is important to note that we are not suggesting that our polymers are forming inclusion complexes with the CDs. Harada and coworkers have previously reported that polyethylene glycol will not form inclusion complexes with β-CDs [23]. However, a valid possibility for these reactions is the ability of α-CDs to cause threading of materials, including PEG [16]. These systems are essentially molecular "nanotubes" where the CD is threaded onto the PEG chains. While β-CDs have been reported to not form inclusion complexes easily with PEG because of their larger size, threading of PEG molecules has been reported with α-CDs [24], and threading of β-CDs has been reported with other hydrophilic materials including ethers, amines, and poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) triblock copolymers (PEG-PPG-PEG) [25, 26]. Therefore, for the reported experiments in solution, it is possible the CD had sufficient time before reaction to form molecular nanotubes with the PEG or the isocyanate endgroup and then was trapped as the material polymerized (Figure 15). This would render a fraction of the CDs unavailable for scavenging contaminants. This might also explain the high degree of ordering observed in the SANS results. This is an observation, previously, unexplained, especially for these rigid polymer systems. A series of CD molecules strung on PEG would be forced to line up and would reduce the scavenging abilities. The only way to validate this theory would be to perform more SANS experiments, including some on the isocyanate:CD (no PEG) systems. This might help explain the inability of the polymers to obtain 100% scavenging but would still not address the wide discrepancy between the PDI and TDI polymer systems, which had ~40–75% scavenging, and the MDI and HDI polymer systems, which had ~5–30% scavenging.

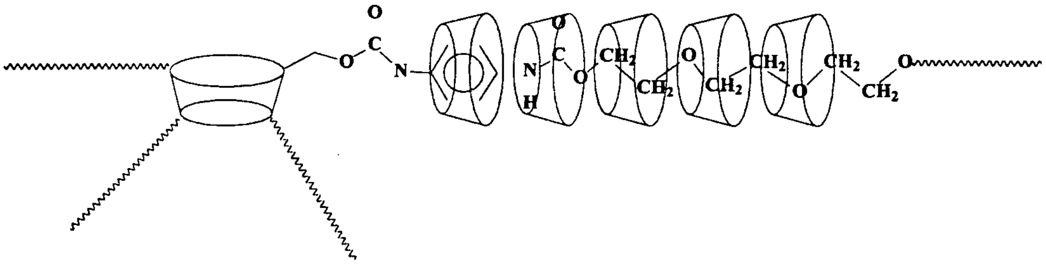
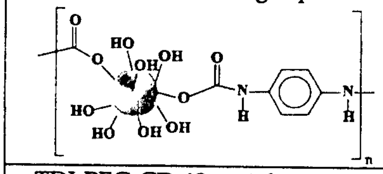
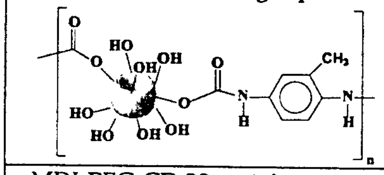
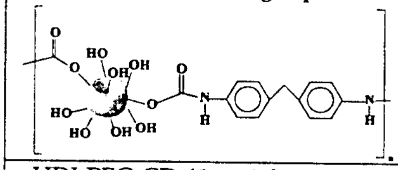
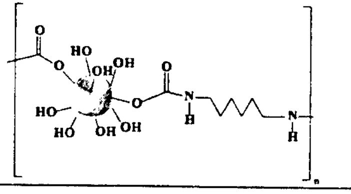


Figure 15. Threading of the CD rings.

For the renewability studies, the working hypothesis based on previous work by other researchers was that CDs would easily release the contaminants, yielding "renewed" materials that could be reused. In these works, no correlation was made based on polymer structure and all renewability studies were performed for an equal period of time. Interestingly, the results were not consistent (Table 5), i.e., the polymers with scavenged TNT did not all release an equal amount of TNT. The tabulated data for the renewability study describes the percent of contaminant recovered from being trapped within the polyurethane-CD. The percentage of contaminant retrieved by the alcohol wash varied with each study performed and with each polymer in the study. In the renewability studies, MDI and HDI polymers performed the best, easily releasing the most contaminant consistently. However, recall that these structures scavenged the least amount of contaminants.

Table 5. Percent contaminant recovered from the renewability studies.

Polymer Sample	Contaminant/Scavenging Time (hr)				
	TNT/3	TNT/18	TNT/44	RDX/3	DMMP/3
PDI-PEG-CD 41-weight-percent 	69%	66%	37%	66%	0%
TDI-PEG-CD 40-weight-percent 	51%	49%	38%	51%	0%
MDI-PEG-CD 32-weight-percent 	86%	81%	23%	90%	0%
HDI-PEG-CD 41-weight-percent 	100%	87%	51%	100%	0%

It is interesting that the 44-hr TNT studies, having the most contaminant trapped within the structure, appear to be the most stable, resisting the release of contaminants. This is not understood. Out of all of the materials, only the HDI-

PEG-CD-41 polymers were fully "renewed." This contradicts predictions and results from previous work by other research groups [12, 13]. Perhaps, while the complexed polymers are stirred in ethanol and the contaminant is being washed out of the CD structure, there still are forces drawing it back into the polymer. It might be more feasible to perform a diffusion wash where the ethanol would flow through the polymer, continuously removing contaminant molecules and preventing rediffusion of the contaminant into the CD. However, it is likely that renewability might be optimized by utilizing a less crosslinked polymer structure where accessibility of the CD molecules are maximized, facilitating both the sorption and desorption of complexed molecules to occur.

UV/Visible spectroscopy can often be performed in coordination with HPLC experiments. UV/Vis is particularly useful because samples are analyzed quickly (in seconds), experimentation is nondestructive to the sample and provides quantitative information regarding concentrations of conjugated molecules in solution. The polymers in our studies contain conjugation and could interfere with a UV/Vis study by causing additional peak appearances. A quick analysis of several polymers in solutions confirmed this. By inserting the polymers in with trapped contaminants into solution and quickly analyzing the results, it was evident that the presence of the conjugation in the polymers was causing the results to be superficially high. Therefore, UV/Vis is not an adequate technique in the analysis of these systems.

4. Conclusions

Structurally unique polyurethane-CD polymers were synthesized, characterized by traditional polymer techniques, and properties evaluated for scavenging ability of contaminants from water and ability to renew the materials through rinsing. Two of the PEG polymers with similar chemical structures (PDI-PEG-CD and TDI-PEG-CD) possessed far greater scavenging capabilities than the other two polymer systems (MDI-PEG-CD and HDI-PEG-CD). A likely cause of this is lack of accessibility of the contaminant to the polymer chains due to reduced polymer free volume combined with CDs possibly threaded onto the polymer chains, rendering them unavailable for scavenging contaminant molecules. Threading of PEG might be a good explanation for the discrepancies between MDI-PEG-CD polymer and the MDI-CD polymer. When PEG was not used in the polymerizations, the scavenging abilities increased significantly.

These issues might be addressed in future work by trying a different chain extender (not polyethylene glycol), by trying to control and therefore reduce the degree of crosslinking, or by using a polymer material possessing greater free volume in a wide range of solvents, such as polyesters. Other future work might include studying the source of the long-range ordering in the system, as observed using SANS. While these materials were neither optimized nor usable directly for applications, a more optimized system could hold promise for improving water treatment technologies.

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13. ABSTRACT*(Maximum 200 words)*

Cyclodextrins are ring-shaped molecules containing an apolar cavity with a diameter 4–8 Å wide and approximately 8 Å deep. Because of the hydrophilic nature of the surface, the materials are readily dispersed in water. However, hydrophobic groups on the inner surface of the nanoporous molecules attract hydrophobic organics that bind noncovalently to the apolar cavity. Recently, polycyclodextrins have been developed as binders for energetic materials and as sorbants for biological materials, and exhibit potential for development as sorbant materials for water filtration. Studies using these polymers have been reported in the literature and show that the polycyclodextrins are very effective scavengers of organic contaminants in water. Our work expands on the use of cyclodextrins in polymers through the synthesis of several organic cyclodextrin-based polymers. These filtering materials have been shown to scavenge several different kinds of contaminants up to parts per million concentrations from water. Some neutron work has been done to try to ascertain the nature of capture of these contaminants.

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