



Microwave-assisted synthesis of cyclodextrin polyurethanes



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ABSTRACT

Cyclodextrin (CD) has often been incorporated into polyurethanes in order to facilitate its use in encapsulation or removal of organic species for various applications. In this work a microwave-assisted method has been developed to produce polyurethanes consisting of α -, β -, and γ -CD and three common diisocyanates. As compared to conventional heating, this new synthetic method saves energy, significantly reduces reaction time, and gets similar or improved yield. The reaction products have been fully characterized with ^{13}C , ^1H , and two-dimensional NMR spectroscopy. With suitable stoichiometry of starting CD and diisocyanate, the resulting CD polyurethane is organic-soluble and water-insoluble and is shown to remove Nile red dye and phenol from water. Possible applications include the removal of undesirable materials from process streams, toxic compounds from the environment, and encapsulation of color or fragrance molecules.

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1. Introduction

Cyclodextrins (CD) are produced from starch through an enzymatic process at a relatively low price (e.g., [Bilensoy, 2011](#); [Easton & Lincoln, 1999](#)). It is known to form inclusion complexes with hydrophobic organic molecules, such as drugs, dyes, flavor, and fragrance molecules. One method to facilitate its use is to produce polymers that incorporate CD (e.g., [Harada, Takashima, & Yamaguchi, 2009](#); [van de Manacker, Vermonden, van Nostrum, & Hennink, 2009](#); [Zhou & Ritter, 2010](#)). Indeed, CD-based polymers have been used in quite a number of applications, including drug delivery, removal of toxic compounds from the environment, removal of cholesterol from food items, the stabilization of volatile or unstable ingredients in foods, encapsulation of fragrance and flavor molecules, and many others ([Chin, Mohamad, & Bin Abas, 2010](#); [Rohrbach, Zemel, & Koch, 1992](#); [Shirasawa, Ueda, Appell, & Goto, 2013](#); [Xiao, Dudal, Corvini, Pieles, & Shahgaldian, 2011](#)).

One of the methods to produce CD-based polymers is to react CD with diisocyanates to form a polyurethane network. Thus, CD dimers and trimers produced from toluene diisocyanate (TDI) and hexamethylene diisocyanate (HDI) were used

in molecular imprinting ([Abbate, Bassindale, Brandstadt, & Taylor, 2012](#); [Hishiya, Shibata, Kakazu, Asanuma, & Komiyama, 1999](#), [Hishiya, Asanuma, & Komiyama, 2002](#), [Khomutov & Donova, 2011](#)). Polyurethanes made from TDI and CD were characterized by IR, DSC and SEM ([Sreenivasan, 1996](#)) and utilized in inclusion complexes ([Rohrbach et al., 1992](#)). Furthermore, TDI-CD polymers were reported to remove paraben from water ([Chin et al., 2010](#)) and HDI-CD polymers were used for its binding with active pharmaceutical ingredients ([Xiao et al., 2011](#)). In all these studies, the CD polyurethanes were produced through conventional heat.

The present authors are interested in the applications of microwave energy for polymer reactions ([Bogdal, 2006](#); [Biswas, Kim, Selling, & Cheng, 2013](#); [Hayes, 2004](#); [Lidström, Tierney, Wathey, & Westman, 2001](#)). In this work, we have found that microwave-assisted reaction is a much more efficient method to produce CD-based polymers. A number of such polymers have been prepared using the microwave-assisted methodology, including the polyurethanes from α -CD/TDI, β -CD/TDI, γ -CD/TDI, β -CD/methanediiphenyl diisocyanate (MDI), and β -CD/HDI. For comparison, the formation of β -CD polyurethanes from conventional heat was also studied. Furthermore, the NMR spectra of these CD polymers were fully assigned.

2. Experimental

The samples of α -, β -, and γ -cyclodextrin were acquired from Acros/Fisher Scientific (Pittsburgh, Pennsylvania). TDI, MDI,

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HDI, and N,N-dimethylformamide (DMF) were all acquired from Sigma Aldrich (Milwaukee, Wisconsin). TDI was specified to consist primarily of 2,4 isomer; only 4% 2,6 isomer was indicated. Dimethylsulfoxide- d_6 (d_6 -DMSO) was obtained from Cambridge Isotope Laboratories (Andover, Massachusetts).

Conventional thermal reaction was carried out on a heating block (Reacti-thermTM from Thermo Fisher, Pittsburgh, PA) with feedback control of temperature. In a typical procedure, 1.0 g CD sample, 0.3 mL TDI (molar ratio of TDI/CD = 2.38), and 5.5 mL DMF were heated at 140–145 °C for a fixed length of time (3–10 min for microwave, 20 min or longer for conventional heat). Samples were recovered by washing three times with ethanol and heated at 60 °C in a vacuum oven overnight.

Microwave-assisted synthesis was conducted on a microwave reactor (Biotage[®] Initiator Microwave Synthesis Systems, from Biotage AB, Uppsala, Sweden). A typical procedure involved the addition into a 10–20 mL Biotage vial, a stir bar, 5.5 mL of anhydrous DMF, and 1.0 g of β -CD. The mixture was stirred for 30 min at room temperature, and 0.3 mL of TDI was added. The Biotage reactor was programmed to pre-stir for 30 s, heat to 145 °C, and hold for 3, 6, or 10 min. The product was transferred into a beaker with ethanol, stirred for 30 min, and then filtered. It was washed three times with ethanol, filtered after each wash, and then dried at 60 °C in vacuo overnight.

NMR spectra were obtained by using DRX 400 spectrometer from Bruker Corporation (Karlsruhe, Germany). The CD polymers were dissolved in d_6 -DMSO, and both ^1H and ^{13}C NMR spectra obtained at ambient temperature. The ^1H and ^{13}C shift reference was tetramethylsilane (at 0 ppm).

Thermogravimetric analysis (TGA) was carried out on a TA Instruments Q500 TGA (TA Instruments, New Castle, Delaware) with nitrogen purge. The sample (7–8 mg) was loaded in an open platinum pan and heated from room temperature to 800 °C at 10 °C/min.

In order to evaluate the sorption properties of the β -CD polyurethane polymers, two studies were conducted. First, β -CD polymers were tested for their binding ability for Nile red dye. The 24 h equilibrium binding assays were carried out on a Labline wrist shaker (setting 7) with 1 mg of polymer in 1.8 mL vials. The results are shown as % Nile red bound for an initial concentration of 0.05 $\mu\text{g mL}^{-1}$ Nile red in 10 mM CaCl_2 (1 mL, pH 5.5). Nile red levels were determined as previously described with the following modifications (Lamprecht & Benoit, 2003). The supernatant containing the free Nile red was filtered through 0.2 μm PTFE syringe filter prior to HPLC analysis. Analysis was conducted using a Shimadzu HPLC system consisting of a LC-20AT pump, Rheodyne injector, SPD-M20A photodiode array detector, CBM-20A control module, DGU-20A₅ degasser, and a Phenomenex Luna 5 μm C18 (2) 100A column (250 \times 4.6 mm²). The mobile phase consisted of 97:3 methanol:water with a flow rate of 1 mL min⁻¹, and the Nile red levels were determined by peak area at 560 nm (0.05–0.002 $\mu\text{g mL}^{-1}$, $R^2 = 0.991$).

In the second study, sorption isotherms were developed for phenol using 24-h equilibrium binding assays. Phenol (2–0.2 $\mu\text{g mL}^{-1}$) in 10 mM CaCl_2 (pH 5.5) was incubated with 5 mg of β -CD polymer in a 1.8 mL screwcap vial on a Labline wrist shaker (setting 7) for 24 h. Phenol levels were determined by HPLC-UV detection using the previously described system with the following modifications (Busto, Olucha, & Borrull, 1991). The mobile phase consisted of 60:40 water/methanol with a flow rate of 1 mL min⁻¹. Free phenol levels were determined based on peak area at 275 nm (elution at 10.8 min). The calibration curve was developed between 2 and 0.05 $\mu\text{g mL}^{-1}$ ($R^2 = 0.996$). Bound phenol levels were calculated through the relationship: $q_e = (C_0 - C_e)(Vm^{-1})$, where C_0 is the initial concentration of phenol, C_e is the concentration of free phenol at equilibrium, V is the volume of the solution, and m is the mass of

Table 1

Polyurethane formation via conventional heat at 140 °C, 30 min, done with 1 g of β -CD in 5.5 mL DMF.

Sample	TDI (g)	TDI/CD, molar	Pyridine (mL)	Yield (%)
A-1	0.243	1.59	0.02	22
A-2	0.243	1.59	0	31
A-3	0.364	2.38	0.02	59
A-4	0.364	2.38	0	61

sorbent. The linear Freundlich equation applied in the analysis is $\log(q_e) = \log(K_F) + (1/n)\log(C_e)$, where K_F is the Freundlich adsorption constant and $1/n$ is the Freundlich exponent.

3. Results and discussion

In order to produce a soluble polymeric product out of CD and diisocyanate, the stoichiometry and the reaction temperature are important parameters. The diisocyanate used in this work has a functionality of two, but CD has 3 hydroxy on each glucose residue, giving rise to multiple reactive hydroxyl groups. Thus, it is easy to get a crosslinked structure if not enough care is taken. Fortunately, the thermal reaction of β -CD and TDI has been studied before (Rohrbach et al., 1992; Sreenivasan, 1996). In their studies, Rohrbach et al. looked at the molar ratio of TDI/ β -CD and found the polymer product to be insoluble in pyridine when the TDI/ β -CD ratio exceeds 2.55. The yield appeared to be around 61%. In view of this finding, we carried out a first study where β -CD and TDI were mixed in two molar ratios (TDI/ β -CD = 1.59 and 2.38), just below the insoluble ratio, at 140 °C in a heating block for 30 min with and without pyridine. The results (Table 1) show that pyridine did not improve the yield. However, the higher TDI level did improve the yield. We decided therefore to use the higher ratio of TDI/ β -CD.

3.1. Microwave-assisted polyurethane formation

In view of our interest in using microwave-assisted methodology, we attempted the reaction of β -CD with TDI by mixing the reactants and heating them in a microwave reactor at the prescribed temperature. A summary of some of the reactions are given in the first three entries in Table 2 (samples B-1 through B-3). It is of interest that at 3-min microwave treatment, the reaction product was a liquid-like material; at 6 min, the product was a partly gel-like solid. No significant change was found at 10 min and a gel-like solid was obtained which was soluble in DMSO. The yield was about the same after 3 min (about 80%). In comparison, for the conventional heat reaction (sample C-1), a reaction time of 20 min was needed, and the yield was slightly lower (73%).

Similar reactions were carried out using microwave-assisted polymerization of β -CD with MDI and HDI. The reactions are summarized in Table 2 (samples B-4 through B-9). Interestingly, all the resulting polyurethanes at the diisocyanate/ β -CD molar ratio of 2.38 gave insoluble products, irrespective of microwave treatment time (3–10 min). Interestingly, the reaction of MDI and β -CD at the same molar ratio (sample C-2) gave a soluble product with conventional heat for 20 min. Nonetheless, the reaction of HDI with β -CD at the same molar ratio with conventional heat (sample C-3) gave an insoluble product.

In order to assess the importance of stoichiometry to product solubility, the various reactions were studied as a function of diisocyanate/ β -CD molar ratio using the microwave treatment at 6 min (Table 3). It is clear that the TDI/ β -CD reaction produces soluble products up to a TDI/ β -CD molar ratio of 2.38 (samples T-1 through T-3). In contrast, the MDI/ β -CD reaction (samples M-1 through M-3) and the HDI/ β -CD reaction (samples H-1 through H-3) produce soluble products only at diisocyanate/ β -CD ratio of 1.19

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