

# Synthesis and characterization of cyclodextrin polyurethane with scavenging properties

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Two kinds of polyurethanes with  $\beta$ -cyclodextrin and amino- $\beta$ -cyclodextrin were synthesized in one step procedure. Their structure was determined by FTIR spectroscopy. Thermal stability and swelling behavior were evaluated. Amino- $\beta$ -cyclodextrin-polyurethane has higher thermal stability than  $\beta$ -cyclodextrin-polyurethane. The swelling degree of  $\beta$ -cyclodextrin product is higher comparing with amino polyurethane, but it is also the subject of the hydrolytic reactions which influence the ability for scavenging. The scavenging properties were studied by static headspace chromatography. In order to prevent environmental pollution, cyclodextrin-polyurethanes can be used as scavenging materials for contaminated solution or atmosphere. This study shows the effectiveness of cyclodextrin-polyurethanes in trapping pollutants.

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## 1. Introduction

Pollution prevention has always been of great interest and scientific research pays more attention to this area. The use of renewable resources to produce polymeric materials was an important step in order to obtain friendly environmental products. Cyclodextrin derivative materials were used to remove organic compounds from contaminated media. The ability of polymeric materials for scavenging has been widely studied [1-7].

Due to the large palette of polyurethane's properties and also due to the existence of hard and soft segments into the polymer structure, these materials can be used in a wide application such as in coatings, fibers, adhesives, sealants. The relationship between structure and properties depends on the molecular chains [8]. Incorporation of renewable resources into the polyurethane chains extends the domain of applications because of low toxicity, biodegradability and high purity [9, 10].

Cyclodextrins (CDs) are one of the most abundant renewable resources produced from starch by enzymatic degradation. CDs have a lot of application in different domains such as food, cosmetic, industry, pharmaceuticals, environmental science [11-15]. CDs comprise a family of cyclic oligosaccharide that contains a number of glucose monomers ranging from six to eight units in the ring:  $\alpha$ -cyclodextrin,  $\beta$ -cyclodextrin and  $\gamma$ -cyclodextrin.  $\beta$ -cyclodextrin is the most used type due to its low cost and accessibility [16]. The most important property of CDs is its central cavity which provides the incorporation of hydrophobic molecules such as organic compounds. Thus results the formation of a host-guest complex [11, 17]. In order to use the ability of CDs in trapping pollutants, they have to be converted into highly

cross-linked polymers, because of the water solubility of CDs [18].

The first application of polyurethane based cyclodextrins was for separating different solvent and aromatic amino acids from chromatography columns. [19-21]. Almost 20 years later, it was reported the synthesis of novel nanoporous polymers made from PUs incorporating CDs [18, 22].

More recently,  $\beta$ -cyclodextrin urethane based polymers were used to remove azo dyes from aqueous solution [23].

Cyclodextrins can also be used in polymer blends to enhance the biodegradation of polymeric materials without affecting mechanical properties [24].

Most synthesis of polyurethane based CDs were performed, till now, through the direct reaction of diisocyanate (MDI, HDI, TDI) with cyclodextrin without using a polyol soft segment. The resulting polymers were used to evaluate the ability to remove organic compounds from aqueous solution [4, 6, 23, 25].

In this study, we synthesized a polyether urethane using CDs as cross-linkers for utilize it as scavenging materials to remove different organic compounds from water and air. These polymers were characterized by Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), swelling study and static headspace gas chromatography (SHGS). Testing the properties of polymers shows that cyclodextrin-polyurethanes can be used to prevent pollution from contaminant solution and atmosphere with toluene, mentone and linalool.

## 2. Experimental

### 2.1 Materials

All chemical used in this study was used as received from the suppliers. The polyether diol was polyethylene glycol (PEG); it had an average molecular weight of 600g/mol and was obtained from Aldrich. 1,6-hexamethylene diisocyanate (HDI), p-toluene sulphonyl chloride (TsCl) and triphenylphosphine ( $\text{PPh}_3$ ) were purchased from Fluka.  $\beta$ -cyclodextrin ( $\beta$ -CD), copper sulphate ( $\text{CuSO}_4$ ), sodium azide ( $\text{NaN}_3$ ) were provided by Aldrich. Sodium hydroxide ( $\text{NaOH}$ ), acetonitrile ( $\text{CH}_3\text{CN}$ ), hydrochloric acid ( $\text{HCl}$ ), N, N-dimethylformamide (DMF), triethylamine (TEA) were obtained from Sigma Aldrich.

In this paper we synthesized two polyether urethane one with pure  $\beta$ -cyclodextrin ( $\beta$ -CD) and the other using 6-amino- $\beta$ -cyclodextrin (NCD) which has been synthesized in our laboratory. 6-Amino- $\beta$ -cyclodextrin was synthesized according to previous reported procedures [26]. Briefly, 6-amino- $\beta$ -cyclodextrin was prepared via a three step process involving a regioselective tosylation of  $\beta$ -cyclodextrin, following by the displacement of tosyl group with  $\text{NaN}_3$  and finally the reduction of the azido group using the Staudinger reduction (Fig. 1).

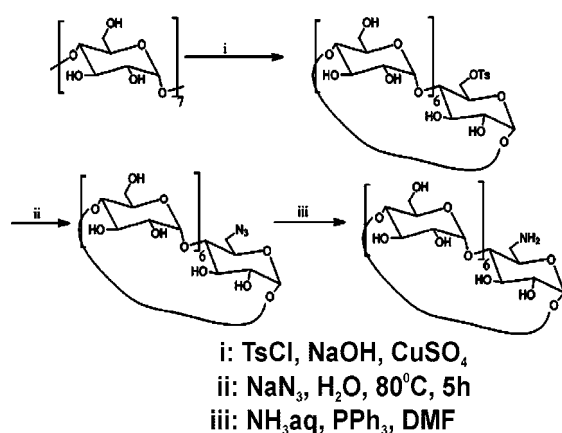


Fig. 1. Three step synthesis of 6-amino- $\beta$ -cyclodextrin.

### 2.2 Polyurethane synthesis

The polyurethanes were prepared by DMF solution polymerization using one-step procedure. The polyether diol was first dried for 2 hours at  $120^\circ\text{C}$  under high vacuum. The macrodiol, diisocyanate and  $\beta$ -CD or NCD, respectively were added into the reactor and the synthesis of PUs was performed at normal pressure, under a nitrogen blanket and vigorous agitation. Triethylamine was used as catalyst in the synthesis. The disappearance of the isocyanate stretching band at  $2200\text{--}2300\text{ cm}^{-1}$  marks the end of the reaction. The resulting material was kept 14 hours at  $60^\circ\text{C}$  and 2 hours at room temperature. The

sample obtained with  $\beta$ -CD was noted with PU1 and that obtained with NCD with PU2.

### 2.3 Measurements

The FTIR spectra were recorded on a Bruker VERTEX 70 Instruments equipped with a Golden Gate single reflection ATR accessory. The spectra were recorded in the range of  $600\text{--}4,000\text{ cm}^{-1}$  with a nominal resolution of  $4\text{ cm}^{-1}$ .

The thermal stability of PUs was tested in an air atmosphere by thermogravimetric analysis (TGA) using a DERIVATOGRAF Q-1500 D apparatus (Hungary). The rate of TGA scans was  $10^\circ\text{C}/\text{min}$ . The initial weight of the samples was about 50 mg and the temperature range was  $30\text{--}700^\circ\text{C}$ .

Swelling behavior of the polyurethanes was evaluated by measuring the amount of water that each polymer absorbs at room temperature ( $25^\circ\text{C}$ ). After measuring their dry weight, samples were placed in 100 ml Erlenmeyer flasks with distilled water. To compare the results, the initial weight of the two samples was the same. The samples were measured during of 10 days, wiped with filter paper to remove any excess water on the surface and weighted. The swelling degree (SW) was calculated using the following formula:

$$SW = \frac{m_w - m_d}{m_d} \times 100 \quad (1)$$

where  $m_d$ ,  $m_w$  were the weights of dry and wet samples, respectively.

#### Static headspace

Measurements were conducted with an Agilent headspace auto-sampler. Sample solutions (using distilled deionised water) of  $10\ \mu\text{l}$  containing different contaminants of  $10^4\text{ ppm}$  were introduced into 22 mL headspace vials and sealed using silicone septa and aluminum foil. The vials were then thermostated at  $30 \pm 0.1^\circ\text{C}$ . After the equilibrium was established (30 min), 1 mL of vapour from the above solution was withdrawn from the vial using a gas-tight syringe and injected directly in the chromatographic column via a transfer line ( $250^\circ\text{C}$ ). Each sample was then analyzed by gas chromatography (Perkin Elmer Autosystem XL equipped with a flame-ionization detector using a DB624 column). The GC (gas chromatography) settings were set as follows: detector temperature,  $280^\circ\text{C}$ ; column temperature,  $120^\circ\text{C}$  for linalool and mentone;  $80^\circ\text{C}$  for toluene. Absorption capacity of the each polyurethane was determined.

## 3. Results and discussions

FTIR spectroscopy was used to investigate the structure of the polyurethanes. The FTIR spectra of the polyurethanes are shown in Fig. 2.

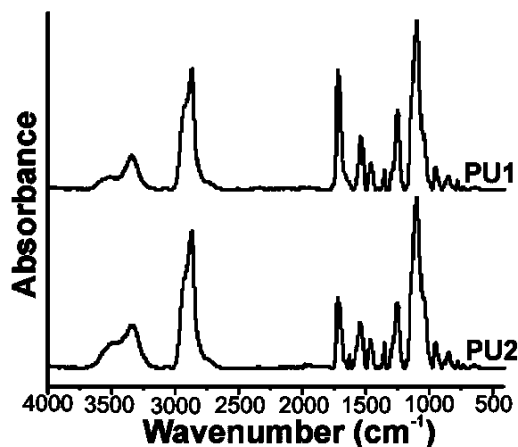


Fig. 2. FT-IR spectra of the polyurethanes synthesized.

The NH and CO regions comprise absorption bands of hydrogen and non-hydrogen bonds. It is well known that in polyurethane hydrogen bonds are in large amounts and they are formed between hard segments or hard segment-soft segment. The presence of them leads to the shift of the characteristic absorption of NH, CO functional groups to lower frequency [27, 28].

The typical bands for polyurethanes are: -NH stretching vibration at 3200-3600  $\text{cm}^{-1}$  (free and bonded), -CH<sub>2</sub> stretching vibration at 2600-3000  $\text{cm}^{-1}$ , carbonyl C=O stretching vibration at 1640-1770  $\text{cm}^{-1}$ , 1500-1600  $\text{cm}^{-1}$  amide II and COC stretching vibration at 982-1200  $\text{cm}^{-1}$ .

In the NH region, the bands centered at 3340  $\text{cm}^{-1}$  (PU1) and 3331  $\text{cm}^{-1}$  (PU2) were assigned to NH hydrogen bonded and the free NH groups appeared as a shoulder at 3504  $\text{cm}^{-1}$  for PU1 and 3483  $\text{cm}^{-1}$  for PU2. The NH band is more intense in case of NCD polyurethane which is in accordance with the higher hydrogen bonding for urea groups. NH bands can be also observed in the finger-print region at 1535 (PU1), 1541 (PU2) and 1247 (PU1), 1249  $\text{cm}^{-1}$  (PU2) assigned to amide II and amide III bands ( $\delta(\text{N-H}) + \nu(\text{C-N})$ ). These bands make additional proof for the formation of urethane structure [29].

In the 1700  $\text{cm}^{-1}$  stretching vibration region, we observed the band associated with hydrogen-bonded C=O stretching vibration at 1715  $\text{cm}^{-1}$  (PU1) and 1716  $\text{cm}^{-1}$  (PU2). Formation of urea linkage in case of NCD-polyurethane is demonstrated by the band at 1623  $\text{cm}^{-1}$  which corresponds to the hydrogen-bonded urea carbonyl. The intensity of bands in the C=O region is lower for PU2 which means that the amount of urethane bonded carbonyl decreases when urea linkage is formed.

The ether region shows a peak centered at 1096  $\text{cm}^{-1}$  (PU1) and 1098  $\text{cm}^{-1}$  (PU2) with no shape difference due to the use of the same polyether diol in the synthesis.

### 3.1 Thermogravimetric analysis

Fig. 3 shows the degradation profile of the cyclodextrin polyurethanes with variation of cross-linking agent. The onset degradation temperature ( $T_i$ ) for PU1 is

lower than that for PU2 (220  $^{\circ}\text{C}$ , 305  $^{\circ}\text{C}$ , respectively) suggesting that  $\beta$ -cyclodextrin is less stable than amino derivative which contains a large amount of water that evaporates first at 100  $^{\circ}\text{C}$ . The degradation usually starts at the urethane bond [30, 31] which is the most labile bond. In the temperature range 200-300  $^{\circ}\text{C}$ , the weight lost for PU1 is 15%, while for PU2 is 8%. The explanation is the higher cross-linking degree of amino- $\beta$ -cyclodextrin-polyurethane (with higher hydrogen bonds due to the presence of urea groups) which is much better evidenced in the main degradation temperature range 300-500  $^{\circ}\text{C}$ .  $\beta$ -Cyclodextrin-polyurethane has a higher amount of weaker urethane bonds and its thermal stability is lower than its homologue. In DTG curves of polyurethanes, there are two degradation steps in 300-500  $^{\circ}\text{C}$  range for PU1, a maximum at 330  $^{\circ}\text{C}$  and the other at 405  $^{\circ}\text{C}$ . Instead PU2 has only one degradation step with a maximum centered at 395  $^{\circ}\text{C}$ , due to the higher physical cross-linking.

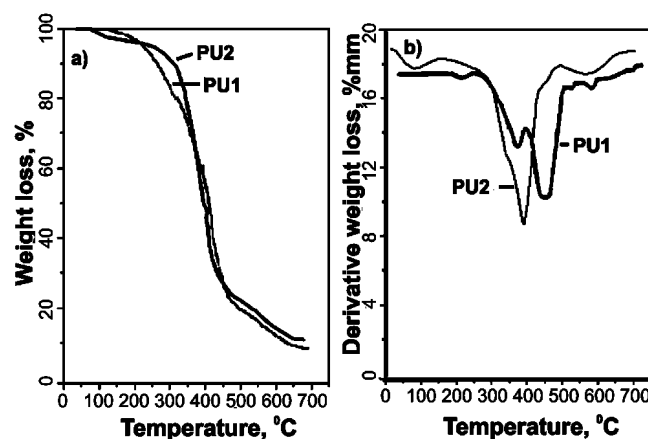


Fig. 3. TGA(a) and DTG(b) curves of  $\beta$ -CD-polyurethane and amino- $\beta$ -CD-polyurethane.

The soft segments of polyurethanes are made up of PEG, so the structures of the polyurethanes are different only in the hard domain. Thus the initial degradation depends on the hard segments structure and the urethane linkage degraded first; the second step of degradation is associated with the soft segment degradation which started at about 300-400  $^{\circ}\text{C}$ . Due to the hydrogen bond formation, the interaction between hard and soft segment in NCD-polyurethane will be stronger and thus thermal stability of amino-polyurethane is higher.

### 3.2 Swelling behavior

The swelling degree in water of the polyurethanes depends sensitively on chemical composition. In swelling study it has been observed that swelling of PU1 is higher than PU2 (Fig. 4) and it also takes more time to reach maximum degree of swelling. Initially up to 1 day for PU2 and 4 days for PU1 swelling increases with time and after that it shows a decreasing trend due to the effect of degradation of polymer chain.

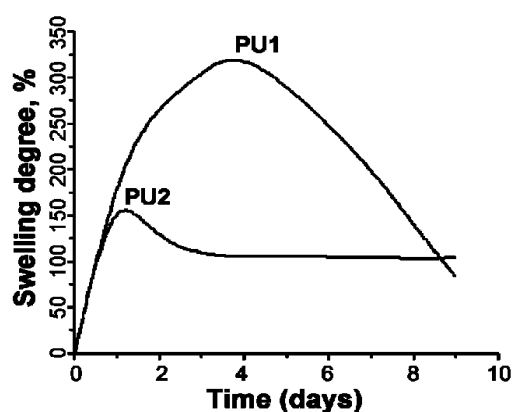


Fig. 4. Swelling of polyurethanes vs. immersion time in water.

NCD decreases the maximum swelling degree of amino-polyurethanes from 320% for PU1 (reached in 4 days) to 156% for PU2 (reached in 1 day). After 4 days BCD-polyurethane reached the maximum swelling, while amino derivative has reached the equilibrium, swelling degree being 106%.

The  $\beta$ -cyclodextrin polyurethane is affected more by the hydrolytic reactions than its amino homologue even if the swelling degree is higher. After 9 days, the weight loss for PU1 is of 55.5% and for PU2 is of 16%. Amino-polyurethane has a higher cross-link density than BCD-polyurethane and thus is more rigid and the possibility of water molecule to penetrate the polyurethane film decreases and also is less susceptible to degradation.

Thus it is expected that scavenging ability to be lower comparing with amino- $\beta$ -cyclodextrin polyurethane (as we'll see from the headspace chromatography measurements).

### 3.3 Headspace chromatography

To evaluate the absorption capacities of our polyurethanes we used static headspace chromatography (HSGH). Absorption efficiencies can be determined through the integration of the desorption curves. It can be seen from Fig. 5 that the absorption capacity of the samples depends of the type of medium that contains the contaminants.

In air atmosphere (a) the scavenging properties are better than in solution (b) for all three contaminants: toluene, mentone and linalool. PU2 has a slightly higher absorbing capacity than PU1 in air and in water, too. As we saw from the swelling measurements, the hydrolytic reactions in case of PU1 was higher so it was expected that the scavenging properties of PU1 to be lower. The binding between CDs and contaminants depends on the hydrophobicity of the guests.

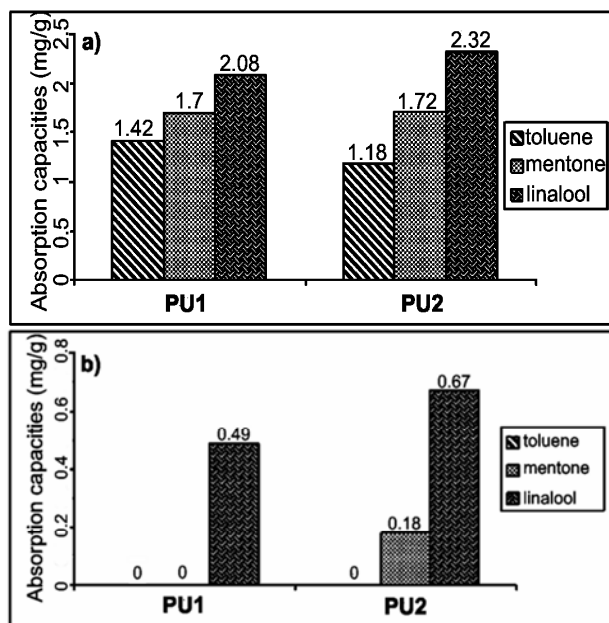


Fig. 5. Absorption capacities (mg/g) for PU1 and PU2 in contaminated atmosphere (a) and contaminated solution (b).

To apply our polyurethane to prevent contaminated solution the use of amino- $\beta$ -cyclodextrin polyurethane is more appropriate than  $\beta$ -cyclodextrin polyurethane.

## 4. Conclusion

Polyurethane materials were synthesized in one step procedure using polyethylene glycol as soft segment and HDI and BCD or NCD as hard segment. The effect of cross-linker nature on thermal stability and scavenging capacities were evaluated. Thus, amino- $\beta$ -cyclodextrin polyurethane showed better thermal stability and scavenging properties than  $\beta$ -cyclodextrin polyurethane.

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