

*Dedicated to the memory of  
Academician Bogdan C. Simionescu (1948–2024)*

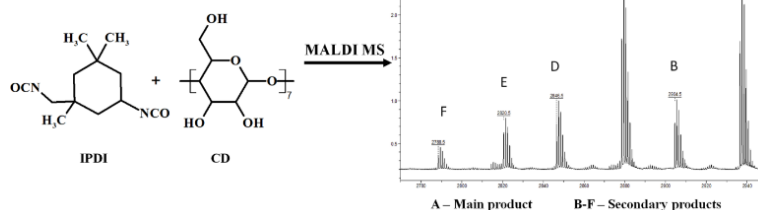
## THE INVESTIGATION OF $\beta$ -CYCLODEXTRIN DERIVATIZATION WITH ISOPHORONE DIISOCYANATE THROUGH MALDI MASS SPECTROMETRY

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The reaction between  $\beta$ -cyclodextrin ( $\beta$ -CD) and isophorone diisocyanate (IPDI) offers a facile approach for synthesizing CD-reactive compounds, enabling the development of advanced materials for environmental, biomedical, and pharmaceutical applications. The resulting products retain highly reactive isocyanate groups, facilitating further chemical modifications. This study investigates the synthesis process using matrix-assisted laser desorption/ionization mass spectrometry (MALDI MS) and nuclear magnetic resonance (NMR) spectroscopy, focusing on the influence of key reaction parameters, including the CD/IPDI molar ratio and reactants concentration, on substitution reactions. Special attention is given to structural modifications at the molecular level, such as potential NCO inactivation via intra-molecular interactions with neighboring hydroxyl groups on CD. These findings contribute to the design and development of novel CD-based materials.



### INTRODUCTION

Cyclodextrin-based materials received increasing attention in the past decade for the development of advanced materials for environmental, biomedical, and pharmaceutical applications.<sup>1–3</sup> Thus, many strategies have been designed for the chemical modification of the OH groups. Among these, the reaction between  $\beta$ -cyclodextrin (CD) and isophorone diisocyanate (IPDI) received special attention for the preparation

of various crosslinked CD-based systems.<sup>4–7</sup> The reaction is influenced by the specific reactive moieties involved, such as the hydroxyl and isocyanate groups. More precisely, the OH groups of CD have different reactivities correlated with their nature, primary or secondary, and their steric accessibility (OH3 are considered sterically hindered and consequently less reactive than OH2).<sup>8</sup> Also, the isocyanate NCO groups of IPDI present certain selectivity when reacting with the alcohols.<sup>4,9,10</sup> The occurrence of inter-cyclodextrin

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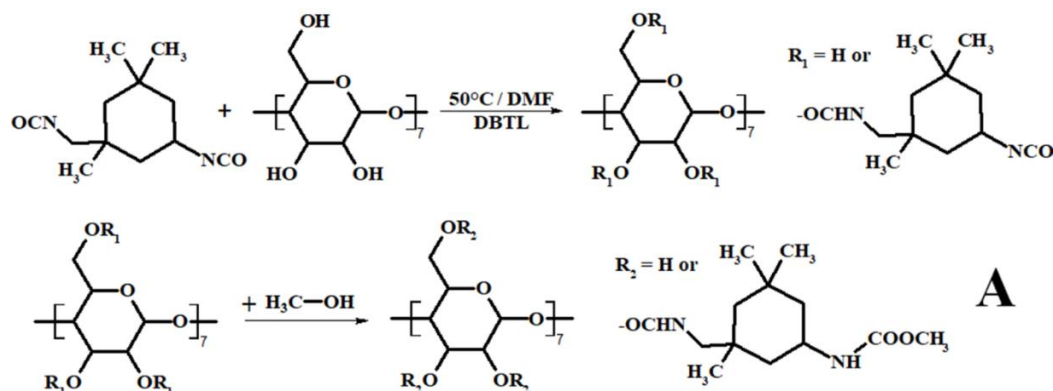
crosslinking represents an intensively employed approach to synthesize polymer networks for various applications.<sup>4,11–16</sup> In some situations, CD is used as a crosslinking agent, but most of the time CD-based materials are envisaged. It is worth mentioning that CD nanosponges, networks based mostly on CD, were first time prepared using the addition of CD OH groups to isocyanates.<sup>17</sup> Thus, depending on the reaction parameters such as CD/IPDI molar ratio, reactants total concentration, temperature, catalyst, etc. the reaction may evolve from CD derivatization to crosslinking. The coupling of polyols is a well-known process, which was previously investigated through size-exclusion chromatography (SEC).<sup>18</sup> Thus, star-shaped NCO-terminated poly(alkyleneoxide) was prepared by avoiding intermolecular crosslinking.

Detailed reaction kinetics of IPDI in the presence of alcohols were performed using various characterization techniques such as Fourier-transformed infrared spectroscopy (FTIR), NMR, titrations, and SEC, etc.<sup>19–25</sup> The preparation of NCO functional macromers using oligomeric diols such as poly(ethylene glycol) or poly(propylene glycol) was also assessed using MALDI MS among other methods.<sup>26,27</sup> However, NCO inactivation processes may also occur at a single

CD molecule level given the presence of neighboring OH groups. Therefore, we further aim to uncover the structural modifications appearing during derivatization with IPDI at the CD molecular level while playing with two reaction parameters, the CD/IPDI molar ratio and the total concentration, respectively.

## RESULTS AND DISCUSSION

The derivatization of CD represents a key step in the preparation of CD-based reactive mixtures for various applications that require CD crosslinking.<sup>4,11</sup> Scheme 1 represents the main reaction pathway leading to IPDI functionalized  $\beta$ -CD. To avoid further product modifications due to secondary reactions before analysis through MALDI MS, the CD-NCO product was subjected to further derivatization of the NCO functional moieties with MeOH. The MALDI MS spectra were acquired using 2,5-dihydroxybenzoic acid (DHB) matrix which is suitable for the analysis of amphiphilic CD derivatives. In the context of MALDI MS analysis, the quenching reaction presents the advantage of revealing whether the NCO moieties are still active, as further described.



Scheme 1 – Schematic representation of the reaction between CD and IPDI with the formation of the main CD-NCO product (A-type structures).

A typical MS spectrum of the quenched product shown in Fig. 1 presents the MS peaks that may be associated with the CD derivatization with IPDI and MeOH. A main series of peaks, with peak-to-peak increment of 254 Da (the mass corresponding to one

IPDI unit quenched with one MeOH molecule) may be associated with A-type structure, CD molecules substituted with a variable number of IPDI monomers quenched with MeOH (structure presented in Scheme 1) and may be described by the following equation:

$$m/z = 1135 (\text{CD}) + n \times 222 (\text{IPDI}) + q \times 32 (\text{MeOH}) + 23 (\text{Na}) \quad (1)$$

For example, the peak found at  $m/z = 1919$  corresponds to a singly charged sodiated adduct (23 Da) composed of one molecule

of CD (1134 Da) substituted with 3 IPDI units ( $3 \times 222$  Da), having the remaining NCO groups quenched with 3 MeOH molecules

(3 $\times$ 32). The spectrum was evaluated taking into consideration the monoisotopic peaks (the theoretical

monoisotopic mass of the CD-NCO structure having substitution degree (SD) = 3 is 1919.8 Da).

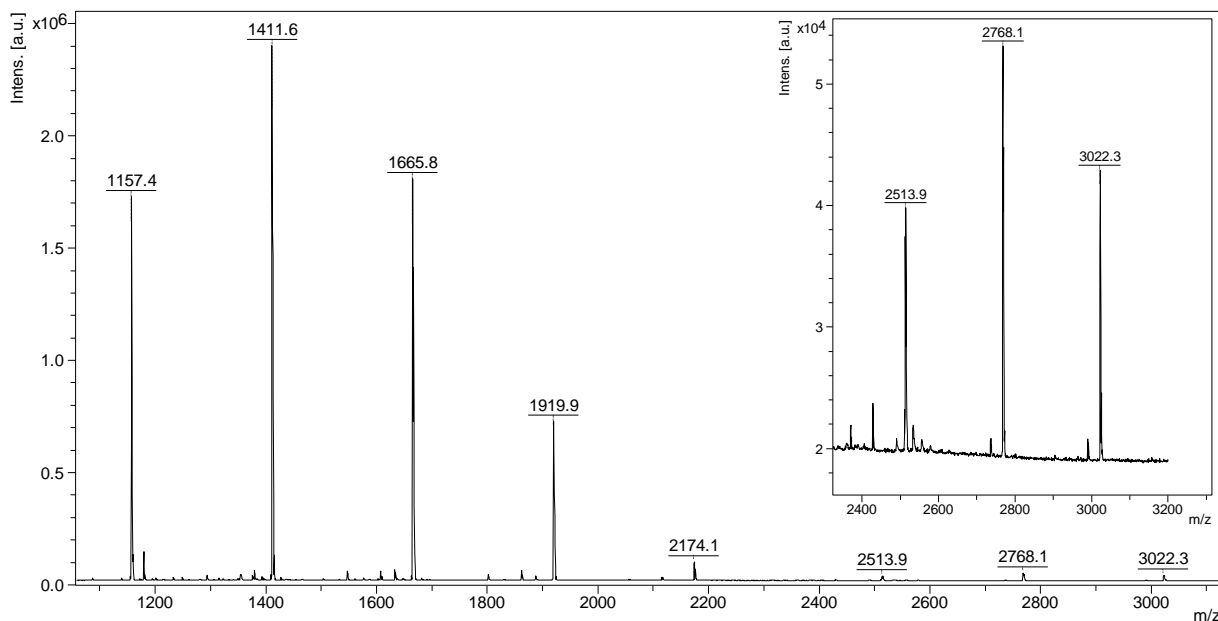
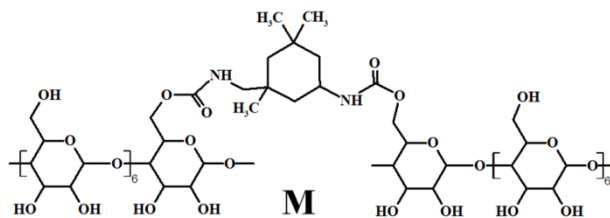


Fig. 1 – MALDI MS spectrum of the CD-NCO sample collected at 15 min, 5% wt., 1/10 CD/IPDI molar ratio.

The spectrum presents in the higher mass region a second series of peaks with a rather low intensity (Fig. 1 highlight) that does not fit the calculations

according to Eq. 1. These peaks are formed through the inter-cyclodextrin coupling of the CD-NCO products (Scheme 2).



Scheme 2 – The inter-cyclodextrin coupling with the formation of M-type structures.

Such coupling reactions may involve more than two cyclodextrin molecules and may be favored by the increasing substitution degree. The

$m/z$  value associated with these CD-NCO products may be inferred from the following equation:

$$m/z = m \times 1135 \text{ (CD)} + n \times 222 \text{ (IPDI)} + q \times 32 \text{ (MeOH)} + 23 \text{ (Na)} \quad (2)$$

For example, the peak found at  $m/z = 3022$  corresponds to a sodiated adduct having  $m = 2$  CD molecules ( $2 \times 1134$  Da),  $n = 3$  IPDI molecules ( $3 \times 222$  Da), quenched with  $q = 2$  MeOH molecules ( $2 \times 32$  Da). This signifies that only two out of theoretically three NCO moieties remain active, one being consumed through inter-cyclodextrin coupling. The intermolecular coupling is a common secondary process when functionalizing polyols with isocyanates. Previously published derivatization of polyols, studied by semiquantitative SEC,

revealed that in the presence of dibutyltin dilaurate (DBTL) and for certain reaction conditions (temperature, solvent concentration and monomer ratio on the feed) only around 10% of the product may be accounted as multiple star coupling<sup>18</sup>. However, in the case of cyclodextrin some difference may be expected. Moreover, supplementary secondary reactions should be taken into account, as further discussed. Therefore, we chose to investigate by MALDI MS the CD-IPDI reaction system by varying the concentration and the molar ratio.

The evolution of the average SD was measured by averaging the MS peaks' intensities in the

corresponding spectra of the reaction fractions collected at the respective reaction time (Fig. 2).

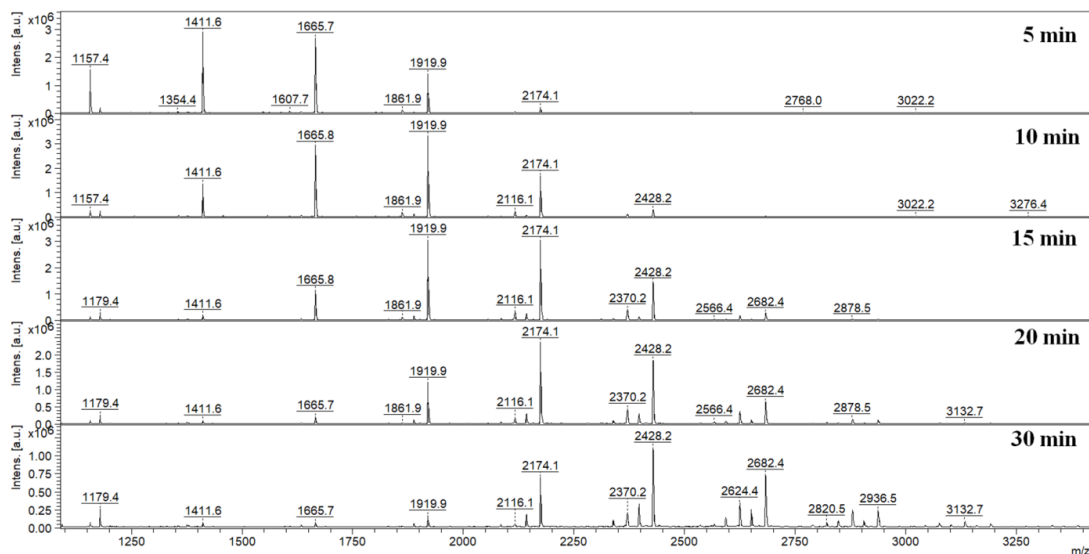


Fig. 2 – The evolution of the CD-NCO product followed by MALDI MS for the reaction system at 15% wt, 1/20.

Thus, we may observe a steady increase in the SD up to 4 IPDI units per CD (the MS peak associated with a CD substituted with 4 IPDI units is located at  $m/z = 2174$ ). However, as the SD reaches higher values, smaller MS peaks accompany the main series, signaling the formation of secondary products. The MS spectrum of the

sample collected at 30 min reveals the secondary peaks that accompany the main peaks (Fig. 3). These peaks are formed during the reaction and they are revealed by the MeOH quenching of the collected samples. In Fig. 3 are annotated the identified secondary peaks and their assignment is detailed in Table 1.

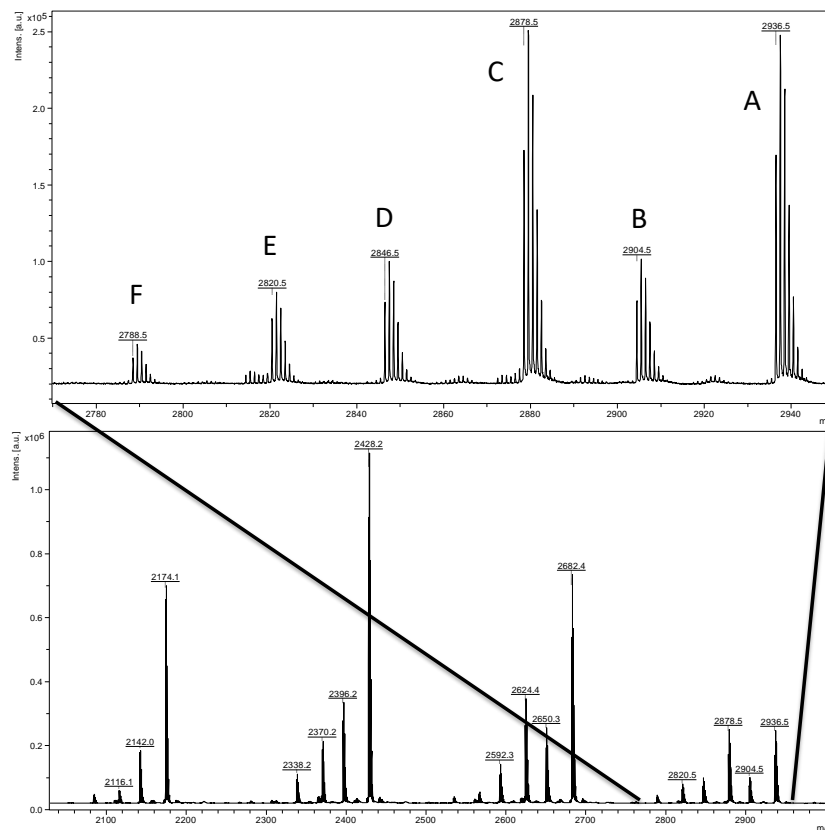


Fig. 3 – Enhanced view of the MALDI MS spectrum (sample collected at 30 min) and the assignment of the MS peaks corresponding to various CD-NCO structures (A–F).

The A series corresponds to the main CD-NCO product, and the  $m/z$  value of 2936 corresponds according to Eq. 1 to a product comprising one CD molecule modified with 7 IPDI units. The B–F peaks

series are associated with CD-NCO products having a similar number of IPDI units, but the number of available NCO moieties is different, as inferred from the mass values and description given in Table 1.

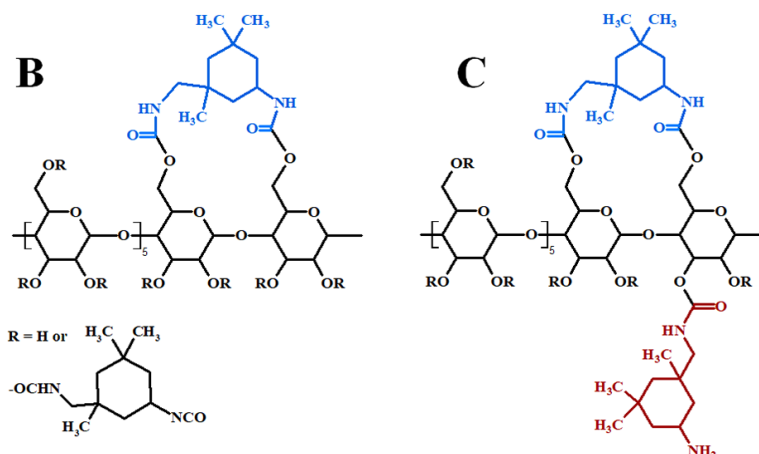
Table 1  
MALDI MS peaks assignment of the A–F peaks

Series	Describing equation	Difference* (Da)	Obs.
A	$2936 = 1135 (CD) + 7 \times 222 (IPDI) + 7 \times 32 (MeOH) + 23(Na)$ .	0	
B	$2904 = 1135 (CD) + 7 \times 222 (IPDI) + 6 \times 32 (MeOH) + 23(Na)$ .	32	1 $\times$ MeOH
C	$2878 = 1135 (CD) + 7 \times 222 (IPDI) + 6 \times 32 (MeOH) + 23(Na) - 26(CO)$	58	1 $\times$ MeOH ; 1 $\times$ NH <sub>2</sub>
D	$2846 = 1135 (CD) + 7 \times 222 (IPDI) + 5 \times 32 (MeOH) + 23(Na) - 1 \times 26(CO)$	90	2 $\times$ MeOH ; 1 $\times$ NH <sub>2</sub>
E	$2820 = 1135 (CD) + 7 \times 222 (IPDI) + 5 \times 32 (MeOH) + 23(Na) - 2 \times 26(CO)$	116	2 $\times$ MeOH ; 2 $\times$ NH <sub>2</sub>
F	$2788 = 1135 (CD) + 7 \times 222 (IPDI) + 4 \times 32 (MeOH) + 23(Na) - 2 \times 26(CO)$	148	3 $\times$ MeOH ; 2 $\times$ NH <sub>2</sub>

\* The difference value is related to the A series

The A to F series correspond to CD-NCO molecules having a similar number of the substituted isocyanate moieties, having the NCO moieties differently consumed, before or during MeOH derivatization reaction. Thus, because some of the NCO moieties substituted to the CD were not available during quenching, the formed derivatives (B–F) had one or more missing MeOH molecules. For example, the B series corresponds to a product that has one less NCO group available. We may hypothesize that the missing NCO group was consumed via the addition of a neighboring OH group (Scheme 3–B). The mass

of products before MeOH derivatization would be described by the equation  $m/z = 1135 (CD) + 7 \times 222 (IPDI) + 23(Na)$ . However, the addition of MeOH allowed us to uncover the fact that one NCO group was previously consumed, by the observation of the missing quenched moiety. Further, the C series, having 26 Da less than the B series, is formed through the reaction of the NCO units with water molecules which results in the transformation of the NCO into NH<sub>2</sub> moieties (Scheme 3–C). Thus, the difference of –26 Da is associated with a loss of 28 Da (CO) and the addition of 2 Da (H<sub>2</sub>).



Scheme 3 – The structure associated with the B and C series observed in the MALDI MS analysis.

This process may occur prior to or during MeOH quenching with the residual water molecules. However, since the quenching process of the samples collected from the reaction at earlier times did not contain urea-modified products, it is safe to assume that most of these secondary reactions are occurring because of the residual water in the

reaction system, before quenching. The newly formed NH<sub>2</sub> moieties are highly reactive towards NCO groups and most probably attack any available NCO function and form urea bonds. Thus, MALDI MS analysis of the A to F series revealed that two main secondary processes occur that lead to a reduction of the NCO groups' number.

Taking into consideration the MALDI MS characterization of the CD-NCO products, we further chose to investigate the optimization of the CD substitution reaction with IPDI, neglecting the formation of M-type of products, which have more than one CD unit in their composition. Thus, three reaction systems were considered where we varied the CD/IPDI molar ratio (P1 – 1/10 and P2 – 1/20 for 5% total concentration) and the total concentration (P2 – 5 % wt. and P3 15 % wt. for 1/20 CD/IPDI molar ratio). The average substitution degree ( $SD_a$ ) values are calculated as the average number of available NCO units per CD molecule, taking also into consideration the prevalence of the secondary products (B-F series). Figure 4a comparative plot of P1/P2 reaction systems confirms that an excess of IPDI leads to higher  $SD_a$  values, similar to P2/P3 increase in concentration. The highest  $SD_a$  was noticed in the case of P3, which

reached a value of about 4 units of IPDI per CD in 20 min reaction time. However,  $SD_a$  does not evidence the effect of the secondary reactions described above. We also represented the progression of the quantity of NCO units that decayed due to intramolecular crosslinking and degradation by water into amines (Fig. 4b). The way the secondary processes influence the SD is described using a parameter called substitution decay (D), which is defined as the percentage of affected NCO groups out of the total theoretical NCO groups corresponding to the number of IPDI units attached to the CD molecule. The D parameter was calculated as the ratio between the relative intensity of the MALDI MS peaks associated with the A series and the relative intensities of all the peaks (series A–F). Therefore, decayed peaks may have a number of available NCO moieties lower than nominal SD (A series), with one or more NCO groups.

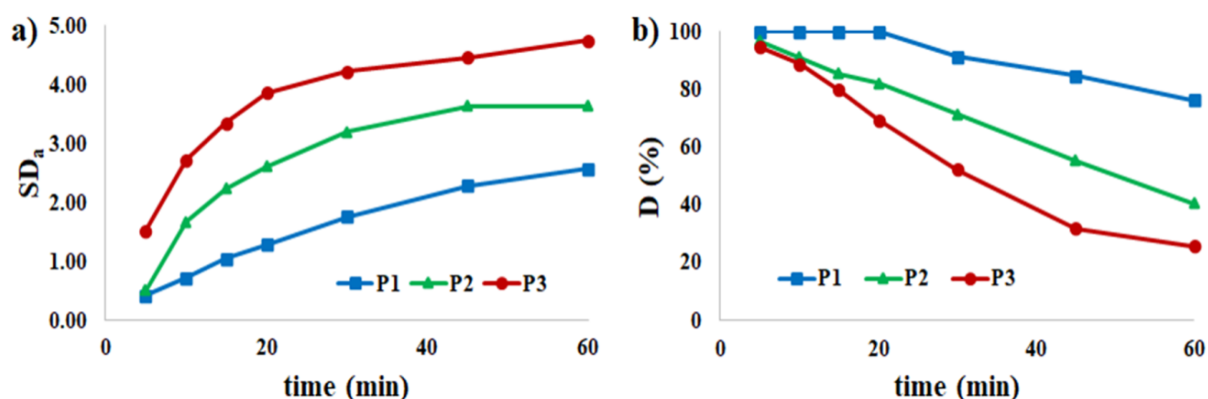


Fig. 4 – Influence of the reaction parameters (total concentration- P2/P3 for 5% wt. and 15% wt. and CD/IPDI molar ratio – P1/P2 for 1/10 and 1/20): a) on the average substitution degree ( $SD_a$ ) and b) decay (D) of the main product  $SD_a$ .

We may observe from Fig. 4b that a significant decay is occurring for increasing concentration or decreasing CD/IPDI molar ratio. Also, the analysis of the reaction conditions revealed that the decay is more prevalent with the increase in the substitution degree. This fact may be also noticed in Fig. 3, from the increase of relative intensity and number of the MS peaks associated with decayed species associated with the substitution degree increase.

Taking the  $SD_a$  parameter into account, we may find an optimum for the reaction conditions in the case of the P3 system, at about 60 min of reaction time that leads to an average of 4.75 NCO units per CD which are available for further reactions. However, more than 60% of these CD-NCO species are affected by decay, thus we may ascertain that a higher number of IPDI units are in fact attached to the CD.

A product collected from the P3 reaction system was isolated and characterized via NMR spectroscopy (Fig. 5), which confirmed the structure and allowed to calculate a substitution degree ( $SD_{NMR}$ ) value around 5.3 IPDI units per CD. As expected, this value is slightly higher than the one obtained through MALDI MS (4.75). The overlapping of the methyl protons from the quenched MeOH (around 3.6 ppm) with the CD protons prevented a more precise NMR evaluation, which differentiates the active NCO moieties. The  $SD_{NMR}$  was calculated using the formula:  $SD_{NMR} = \frac{I_{Hb,f}}{I_{H1}} \times \frac{7}{2}$  where:  $I_{Hb,f}$  is the integral value for the peak from 1.47 ppm attributed to two of the Hb and Hf protons from the IPDI residue and  $I_{H1}$  is the integral value for the peak from 4.88 ppm, attributed to the anomeric protons from cyclodextrin.

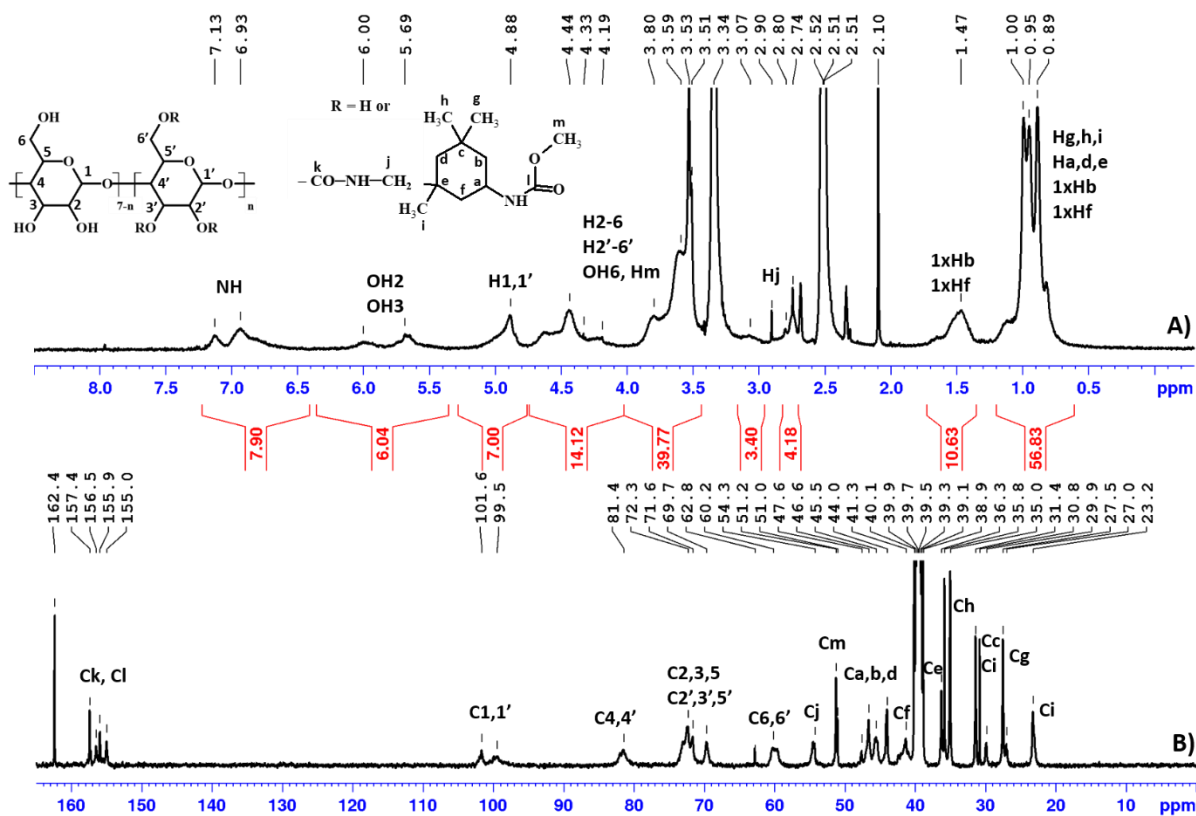


Fig. 5 – a)  $^1\text{H}$  NMR spectrum and b)  $^{13}\text{C}$  NMR spectrum of CD-NCO quenched sample collected at 60 min.

## EXPERIMENTAL

### Materials

$\beta$ -Cyclodextrin (CD – Cyclolab, Budapest, Hungary) was vacuum-dried at 0.01 mbar and 80°C for 72 hours, then stored in a desiccator under an argon atmosphere. Dimethylformamide (DMF – Sigma-Aldrich) was distilled and dried using 3Å molecular sieves. Isophorone diisocyanate (IPDI), dibutyltin dilaurate (DBTL), methanol (MeOH), and diethyl ether (all from Sigma-Aldrich) were used as received without additional purification.

### Synthesis of cyclodextrin derivatives modified with IPDI (CD-NCO)

In a vacuum-dried flask closed with a rubber stopper, 0.1g CD was introduced under the Ar protection together with 0.9 mL DMF and left to homogenize until the solution was clear. Also, 0.185 ml of IPDI monomer and 0.9mL DMF were mixed in a separate vacuum-dried flask. Once the CD solution was homogenized, 3  $\mu\text{L}$  of DBTL were added, and under an Ar atmosphere, the IPDI solution was gradually added dropwise using a gas-tight syringe. Reactives quantities given herein are

for a typical reaction – molar ratio of CD:IPDI of 1:10 and 5% wt. monomers concentration. The monomers amounts were adjusted otherwise. The final reaction mixture was placed in an oil bath and stirred magnetically at 50°C for 1 hour. Samples (20  $\mu\text{L}$ ) were collected at various time intervals, quenched in methanol for 24 hours to deactivate the reactive NCO groups, and then analyzed using MALDI MS. The product obtained after 1 hour (using a molar ratio of CD:IPDI=1:20 and wt %=15%) was purified with diethyl ether and subjected to NMR analysis.

### Characterization methods

The NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer equipped with a 5 mm direct detection probe. The spectra were recorded using DMSO- $d_6$  as solvent, at room temperature, using the standard parameter sets as provided by Bruker. The chemical shifts are given relative to the solvent residual peaks (2.51 ppm for  $^1\text{H}$  and 39.5 for  $^{13}\text{C}$ ). The assignment of the peaks in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra was based on additional 1D and 2D homo- and hetero-nuclear correlation experiments ( $^{13}\text{C}$  DEPT135, H,H-COSY, H,C-HSQC and H,C-HMBC).

<sup>1</sup>H NMR (400.13 MHz, DMSO-d<sub>6</sub>, δ, ppm): 7.13–6.93 (NH), 6.00–5.69 (OH2, OH3), 4.88 (H1, H1'), 4.44–3.59 (H2–6, H2'–6', OH6), 3.53 (Hm), 3.07–2.80 (Hj), 1.47 (1×Hb, 1×Hf), 1.00–0.89 (Ha,d,e,g,h,i, 1×Hb, 1×Hf). <sup>13</sup>C NMR (100.6 MHz, DMSO-d<sub>6</sub>, δ, ppm): 157.4–155.0 (Ck, Cl), 101.6–99.5 (C1, C1'), 81.4 (C4, C4'), 72.3–69.7 (C2,3,5,2',3',5'), 60.2 (C6, C6'), 54.3 (Cj), 51.2–51.0 (Cm), 46.6–44.0 (Ca,b,d), 41.3 (Cf), 36.3 (Ce), 35.0 (Ch), 31.4 (Ci), 29.9 (Cc), 27.5–27.0 (Cg), 23.2 (Ci).

MALDI MS – Mass spectrometry measurements were performed using the RapifleX TOF-TOF instrument (Bruker, Bremen, Germany). The mass spectrometer was operated using FlexControl 4.0 and the acquired spectra were processed with the FlexAnalysis 4.0 software. The MS calibration was performed using poly(ethylene glycol) standards applied to the MALDI MS target in similar conditions to the samples.

Samples from the reaction mixture were directly introduced in excess of MeOH (approx. 1/100 v/v) for 24 h to quench the reactive NCO groups, prior to MALDI MS analysis. The 2,5-dihydroxybenzoic acid (DHB) matrix and NaI solutions were prepared in methanol at concentrations of 20 mg/mL, and, respectively, 5 mg/mL. 20 μL of matrix solution was mixed with 2 μL of NaI and 2 μL of sample solution and 1 μL from this mixture was deposited on the ground steel plate. The spectra were acquired in the positive reflectron mode, and the laser ionization power was adjusted slightly above the threshold to produce consistent MS signals. 6000 spectra were collected from three different regions of the spot for each sample. The obtained MALDI MS spectra were further used to calculate the average substitution degree (SD<sub>a</sub>) according to the specific structural assignment and using the corresponding intensity values of the respective MS peaks. The calculation takes into consideration the effective substitution degree (SD<sub>x</sub>) which is the number of NCO units per CD molecules that were found available through MeOH quenching. SD<sub>a</sub> was calculated using the formula:  $SD_a = \frac{\sum_{x=1}^n SD_x \times I_{px}}{\sum_{x=1}^n I_{px}}$ , where SD<sub>x</sub> is the substitution degree and I<sub>px</sub> is the intensity of the peak *x*. Substitution decay (D) parameter was calculated as:  $\% D = \frac{\sum_1^n I_p}{\sum_1^n I_t} \times 100$ , where I<sub>p</sub> is the intensity of the MS peak of the typical CD-NCO product, and the I<sub>t</sub> are the intensities of all the peaks from the spectra (including secondary CD-NCO products).

## CONCLUSIONS

The modification of CD molecules with IPDI monomer was analyzed by a MALDI MS method that points out besides the formation of the main product, secondary products. Thus, besides the classical inter-cyclodextrin coupling, a well-known problem in grafting reactive moieties on multifunctional core molecules, we were able to detect intramolecular reactions that diminish the number of available NCO functions on the final product. The MALDI MS analysis of the MeOH-quenched CD-NCO samples revealed that NCO moieties are consumed through grafting of the IPDI molecules with both NCO moieties on the CD or by loss of carbon dioxide in the presence of water molecules. The reaction parameters, such as total monomer concentration and CD/IPDI molar ratio, were taken into consideration for the MALDI MS evaluation of the effective substitution degree, defined as the number of NCO groups available per CD molecules. Also, a decay ratio describing the partial loss of the NCO molecules from the CD-NCO product was calculated. The number of the IPDI units attached to the CD was also assessed using NMR. The comparison between the two characterization methods confirmed that NCO units are partially consumed via secondary reactions.

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