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Design and characterization of novel β-cyclodextrin based copolymer materials

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ABSTRACT

Reported herein are the systematic design and characterization of several novel polyurethane (PU) copolymers containing a macrocyclic porogen (β-cyclodextrin; β-CD). These copolymers were synthesized from the reaction between β-CD with different types of diisocyanate linker molecules (e.g., 1,6-hexamethylene diisocyanate (HDI), 4,4′-dicyclohexylmethane diisocyanate (CDI), 4,4′-diphenylmethane diisocyanate (MDI), 1,4-phenylene diisocyanate (PDI) and 1,5-naphthalene diisocyanate (NDI)) at variable synthetic conditions. The copolymers were characterized using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), solid state ^{13}C CP-MAS NMR, $^{1}H/^{13}C$ solution NMR spectroscopy, thermogravimetric analysis (TGA) and elemental analyses (CHN). The PU copolymers were generally insoluble in water and the optimal preparation of copolymer materials for sorption-based applications is for β-CD/linker synthetic mole ratios from 1:1 to 1:3. The practical upper limit of the crosslink density (~1:7, β-CD/linker) depends on the steric bulk of the cross linker units.

1. Introduction

Cyclodextrin (CD) copolymer materials have a wide range of industrial applications because of their unique sorption properties.[1–4] The sustained interest in the research and application of CD-based copolymer materials is attributed, in part, to the ability of such copolymer materials to form host–guest complexes comparable to native CDs.[3,5–9] Technologies that that rely on the formation of inclusion complexes include a wide range of examples such as chemical separations, catalysis, molecular sieves, food processing, pharmaceutical excipients and cosmetics.[1,10–17] In particular, the ability to tune the inclusion properties of CD-based copolymers is an important parameter in materials research and design.

Previous reports have shown that polymeric β-CD materials may function as sorbents for the inclusion of organic molecules from aqueous solutions.[7,8] More recently,[18] it was shown that the systematic variation of the copolymer structure enables tuning of the inclusion site accessibility. The ability to tune the copolymers is critical in cases where the copolymer sorption and molecular recognition involve the formation of CD/guest inclusion complexes.[19] Although, β-CD-based PU copolymers have been prepared previously,[7,18,20] the range of synthetic conditions was limited, as was the selection of diisocyanate cross linkers investigated. The importance of co-monomer composition has been overlooked as evidenced by numerous studies which have employed arbitrary co-monomer ratios for the synthesis of β-CD copolymers.[7,21–23] For example, a common approach utilizes β-CD/co-monomer mole ratios ~1:7. Presumably, this is based on the presence of seven primary hydroxyl groups with moderate reactivity. The use of bulky diisocyanate linkers with mole ratios that exceed 1:7 is considered problematic because extensively cross linked materials may have limited inclusion site accessibility of β-CD. The optimal design of CD-based copolymer sorbents takes into account the nature of the crosslink unit and the relative co-monomer ratios since these parameters will strongly affect the structure of the copolymer framework and its adsorption properties.

In this study, we report the synthesis and characterization of a novel series of β-CD-based copolymer PU materials. The β-CD copolymers contain diisocyanate co-monomers with variable aliphatic and aromatic molecular structure, which varies according to their molecular size and conformational motility (cf. Fig. 1). The copolymer sorbent frameworks have tunable adsorption properties since changes to the co-monomer ratios affect the surface areas, pore size distribution, mechanical properties and surface chemistry of the sorbent. The results of this research will contribute to the development of improved solid phase extraction materials with enhanced sorption and molecular recognition properties.[2,4,24]

2. Results and discussion

2.1. Synthesis

The nomenclature of the copolymers is described according to the type of diisocyanate and the co-monomer mole ratio (β-CD:diisocyanate linker). The diisocyanates investigated include the following:

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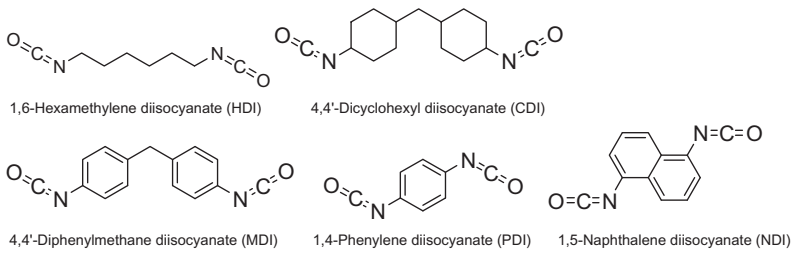


Figure 1. Diisocyanates of variable molecular structure used in the synthesis of copolymer materials.

1,6-hexamethylene diisocyanate (HDI), 4,4′-dicyclohexylmethane diisocyanate (CDI), 4,4′-diphenylmethane diisocyanate (MDI), 1,4-phenylene diisocyanate (PDI) and 1,5-naphthalene diisocyanate (NDI). For example, the 1:3 β-CD:HDI copolymer designation used herein is denoted as HDI-X (X = 3) where the molar quantity of β-CD is assumed to be unity relative to 3 mol of HDI.

The copolymers were prepared by the addition reaction between the primary or secondary hydroxyl groups of β-CD with a bifunctional diisocyanate crosslinker, as shown in Scheme 1. There are numerous hydroxyl groups in β-CD; seven primary and fourteen secondary hydroxyl groups, at the narrow and wide ends of the CD torus, respectively. The yield of the copolymer was observed to increase with greater diisocyanate mole content (X >1) relative to β-CD. In the case of the HDI-X copolymers, the product formed a gel phase at the 1:3, 1:6 and 1:9 mole ratios. The gellation time decreased with an increased crosslink density (X ⩾ 3). The yields are 37% and 62% for HDI-1 and HDI-2 copolymers, respectively, and the greater mole ratios afforded quantitative (∼98–100%) yields. Similar trends were observed for the CDI-X copolymers; however, the gellation time occurred more rapidly at greater linker mole ratios (i.e., X > 1). The yield of CDI-1 was 88%, whereas, CDI-2 and -3 were nearly quantitative. At the 1:9 mole ratio, the reaction was complete, as evidenced by rapid gel formation within an hour. During the solvent removal step, DMA was more difficult to remove at the higher crosslink densities. This observation may indicate the trapping of solvent within the mesopore copolymer framework. For the aromatic-based copolymers, the yield of MDI-based copolymer materials exceeded that for PDI than NDI. The yields for the copolymers with aromatic linkers are given as follows; MDI-1 (76%), MDI-2 (86%), MDI-3 (97%); PDI-1 (62%), PDI-2 (74%), PDI-3 (83%); and NDI-1 (31%), NDI-2 (46%) and NDI-3 (77%). The HDI and CDI-based copolymers were white in color, whereas, MDI- and PDI-based copolymers were a lightly cream colored, and NDI copolymers were light brown in appearance.

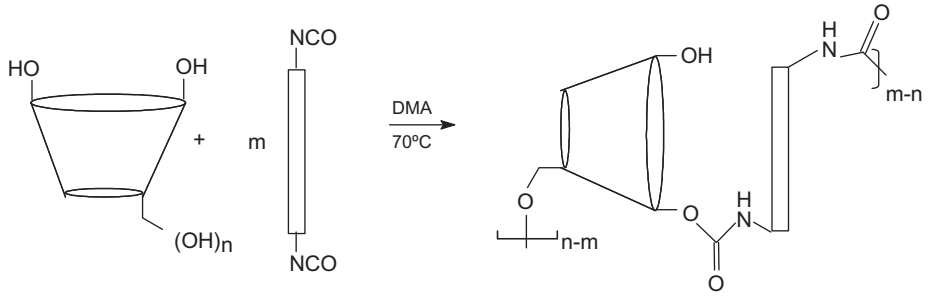
2.2. Characterization

2.2.1. IR

DRIFT spectroscopy was used to assess the spectral signatures of the functional groups in the products prepared according to Scheme 1. Figure 2a–e illustrates the DRIFT spectra for the starting materials; β-CD hydrate and the diisocyanate linkers (HDI, CDI, MDI, PDI and NDI), along with the corresponding copolymers. The IR spectra confirmed the identity of the copolymers as evidenced by the disappearance of the isocyanato group between 2500 and 2080 cm^{-1} and the co-appearance of the amide and carbonyl vibrational bands. The vibrational band of ν(N–H) appears ∼3376 cm^{-1} and overlaps with the broad –OH band from β-CD hydrate.[25] The observed vibrational band for ν(C=O) ranges between 1702 and 1666 cm^{-1}, as shown in Table 1. The rotational/vibrational bands δ(N–H) + ν(C–N) range between 1549 and 1521 cm^{-1} for the aliphatic and aromatic diisocyanate linker units.[25] The relative peak areas (% total) for C=O and C–N vibrational bands are summarized in Table 1. The relative peak area increases as X increases (cf. Table 1) and these results offer a semi-quantitative approach for assessing the relative copolymer composition which contain similar diisocyanate units. A comparison of the relative β-CD/diisocyanate mole ratio combined in the reaction mixture indicates that the IR results further support the formation of urethane bonds as X increases, as described by Scheme 1.

2.2.2. Elemental analyses

CHN elemental microanalyses provided estimates of the linker composition since the N content originates solely from the diisocyanate co-monomers or residual solvent (e.g., DMA) and generally increases as the relative mole ratio (X) increases (cf. Table 2). The increasing N content of copolymer materials with increasing X provides further support for the molecular identity of the copolymer products. Corrections due to residual water and/or solvent mixtures remaining within the copolymer framework were not applied because the relative amounts of residual solvents were not assessed. The overall total contribution of solvent varied from 0.1% to 6%, and was in good agreement with the ^{1}H NMR results where non-deuterated solvent signatures (i.e., DMA, methanol and water) were observed in the ^{1}H spectra (cf. Section 2.2.3). Residual solvents are attributed to the occlusion of solvent within the copolymer framework during the crosslinking and/or purification stages. The presence of residual solvents was previously concluded[26] for an HDI-3 copolymer which showed a markedly different (i.e., 1:1.5) co-monomer ratio using a similar methodology. The



Scheme 1. Generalized formation of a urethane copolymer material via an addition reaction between the hydroxyl groups of β-CD and the bifunctional N=C=O groups of a diisocyanate linker molecule in dimethyl acetamide (DMA) at 70 °C.