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High-resolution solid-state ^{13}C NMR study of per(3,6-anhydro)-α-cyclodextrin based polymers and of their chromium complexes

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Abstract

High-resolution solid-state ^{13}C NMR was employed to characterise polymers made of per-3,6-anhydro-α-cyclodextrins with 1,6-diisocyanato-hexan used to bridge the macrocyles. These materials were designed because of their insolubility and their extractant properties due to the presence of the cyclodextrin rings. The properties of this new type of material appear very promising as potential extractant of different oxoanions. The properties of these materials to bind chromate or dichromate ions appear to be particularly attractive since the extraction of chromium is high and moreover there is no degradation of the polymers that can be further regenerated. These features rely mostly on qualitative and quantitative analyses of CP/MAS spectra. The studies of the NMR relaxation times, T_{CH}, T_{1pH} and T_{1C} for the starting polymers and its metal complexes allowed obtaining valuable insights concerning the molecular sites of interactions of the polymers with the oxoanions.

Keywords: Chromium; Solid-state NMR; Selective extraction; Polymers; Modified cyclodextrins; Relaxation times

1. Introduction

Extraction of metals that are toxic or radioactive from soils or waters has become an important challenge in environmental chemistry (Roundhill, 2001). Numerous approaches have been proposed such as precipitation, electrochemical and complexation methods (Roundhill & Koch, 2002). Polymers made of cyclodextrin derivatives belong to this latter strategy.

Cyclodextrins can be polymerised by reacting their hydroxyl functional groups with a variety of crosslinking reagents. One of the oldest and most widely used crosslinking reagents is epichlorhydrin (Solms & Egli, 1965). Important work on polyurethane cyclodextrins resins has been introduced by Mizobuchi, Tanaka, and Shono (1980). A key objective in the synthesis strategy is that access to the cyclodextrin cavity is not obstructed. Another very important point is that the synthesised material should not be degraded by the oxoanions. For instance, the chromate and dichromate that have a very high toxicity present also a specific problem because they are strong oxidising agents.

On the base of these chemical engineering considerations, polymers made of per-3,6-anhydro-α-cyclodextrins (Gadelle & Defaye, 1991) were retained as materials of potential interest. Moreover, to determine the potential affinity of these polymers in the presence of ions, model compounds, such as per(2-*O*-ethylcarbamate-3,6-anhydro)- and per(2-*O*-hexylcarbamate-3,6-anhydro)-α-cyclodextrin, have been synthesised. These products have been rapidly screened with metallic anions and cations on resin plates (Cadars, Foray, Bayle, Gadelle, & Bardet, 2002). These molecules, soluble in water, did form complexes with chromate and dichromate. On the base of the above exploratory results, our strategy reported in the present work has been to prepare and to study polymers resulting from the reaction of per(3,6-anhydro)-α-cyclodextrin with

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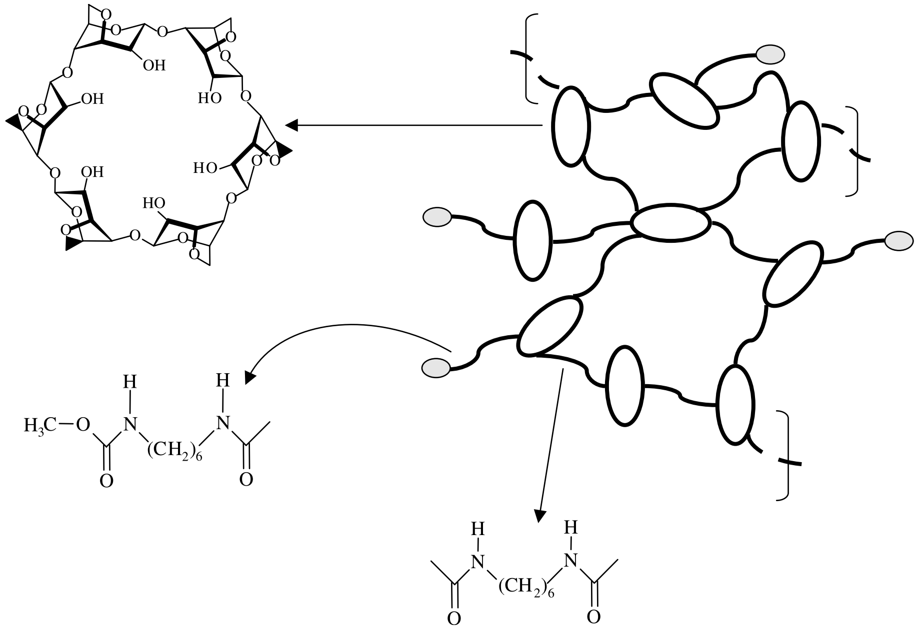

Fig. 1. Schematic representation of the starting polymer $(CD)_x(DIH)_y$. Abbreviations: CD, 3,6-anhydro-α-cyclodextrin; DIH, 1,6-diisocyanato-hexan.

1,6-diisocyanato-hexan, respectively, abbreviated CD and DIH. Different amounts of CD and DIH, respectively, x and y, have been used to synthesise the polymers. The resulting copolymers are designated as $(CD)_x(DIH)_y$ in this paper. An important step in the syntheses of these polymers is the destruction of residual isocyanate groups in methanol to quantify the number of isocyanate groups. It allows the preparation of polymers free of such end groups (Vincendon, 1993). A schematic representation of the expected structure for theses synthetic copolymers is shown in Fig. 1.

Moreover, as mentioned above, chromate or dichromate presents a particular problem because it is a strong oxidising agent. In the per(3,6-anhydro)-cyclodextrins, the inversion of conformation of all D-glucopyranose rings from the $^4C_1$ to $^1C_4$ prevents from the oxidation of the molecule.

Our polymers insoluble in water have been tested in the presence of solutions of potassium chromate and dichromate. All samples were stirred with large amounts of metal solution then carefully washed with water (three times) and dried at room temperature. Residual water was quantified by thermogravimetry.

High resolution solid-state NMR is a powerful tool to characterise the structure of polymers (Komoroski, 1986; Ngono-Ravache, Foray & Bardet, 2001) and to study their motions (Schmidt-Rohr & Spiess, 1996; Voelkel, 1988). In this study, we have combined both a classical structural study and a molecular dynamic study. Structural analyses are based on chemical shift analyses and quantitative treatments of the data. A more complex approach concerns the interpretation of relaxation time measurements of the different synthesised polymers and those of their complexes. This aspect involves mainly the cross-polarisation times, T_{CH}, the proton spin–lattice relaxation times in the rotating frame, $T_{1\rho H}$, and the carbon spin–lattice relaxation times T_{1C}. The molecular dynamic studies through relaxation parameters determined by NMR are directly correlated with motions inside the materials. Moreover, they are sensitive to different motional frequencies, over some decades. This renders the NMR technique particularly powerful since the events that underwent the polymers can be analysed on different structural levels; starting from local molecular modifications up to overall aspects of the polymers such as its backbone mobility (McBrierty, 1997).

2. Experimental

2.1. Polymer syntheses and chromium complex preparation

α-Cyclodextrin was a gift from Wacker (France). 1,6-Diisocyanato-hexan (DIH) was purchased from Aldrich (USA). Both reagents were used without further purification. DMF was distilled before use. Per 3,6-anhydro-α-cyclodextrin was prepared according to Gadelle and Defaye (1991). This compound is abbreviated CD.

Two starting polymers from 3,6-anhydro-α-cyclodextrin (CD) and 1,6-diisocyanatohexan (DIH) were synthesised. As they differed only by their relative content in both constituents, we used the following abbreviation, $(CD)_x(DIH)_y$, where x and y indicate the respective molarity of the mixture used before polymerisation. Our cyclodextrin polymerisation concerns only low molecular CD oligomers ($MW \leq 10{,}000$). Reactive groups were only secondary alcohol. This information was obtained by circumstantial evidence from others copolymers studied by mass spectrometry. Using these