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Synthesis and solid-state NMR study of chromium complexes of per(3,6-anhydro)-α-cyclodextrin based polymers

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Abstract

This work presents the synthesis strategy, the structural characterization and the molecular dynamic properties of decontaminant polymers based on modified cyclodextrins. The polymers were made of per(3,6-anhydro)-α-cyclodextrin with either 2,4-diisocyanatotolylene, 1,4-diisocynatophenylene, 1,6-diisocyanatohexane or 1,12-diisocyanatododecane to bridge the modified cyclodextrin moiety. On the starting polymers and their metal complexes, the structural studies were carried out using classical 1D and 2D solid-state NMR experiments such as 2D WISE, along with the measurements of the time constants T_{CH}, $T_{1\rho H}$ and T_{1C}. Information obtained on the changes in mobility of these different starting polymers gives insights into their ability to extract dichromate. The molecular sites of interactions between the oxoanions and the polymers could be also determined from these experiments and appear to be dependant upon the nature of the cross-linking agents.

Keywords: Molecular dynamics; Polymers; Dichromate; Solid-state NMR; Modified cyclodextrins

1. Introduction

Decontamination is a subject of great environmental interest and has become an active field of research for the last 20 years (Mizobuchi, Tanaka, & Shono, 1980; Roundhill, 2001; Roundhill & Koch, 2002). The synthesis of polymers containing chemical groups with specific complexation properties leads to materials which can be used to extract toxic or radioactive metals. This paper deals with polymers based on modified cyclodextrins. They are of particular interest because of their insolubility and their properties to extract metallic oxoanions present in contaminated water. In a previous paper (Cadars, Foray, Gadelle, Gerbaud, & Bardet, 2005), we have studied the localization of chromate or dichromate oxoanions within polymer made of per(3,6-anhydro)-α-cyclodextrin (CD) units linked together with 1,6-diisocyanatohexane (DIH). We concluded that chromate lies outside the cavities of the modified cyclodextrins, while dichromate is complexed inside the cavities.

On the base of these results a specific chemical engineering strategy has been explored in order to investigate different types of materials keeping in mind that the modified cyclodextrin, CD, has to be the core of these new materials. Indeed, all the tests performed on the modified CD alone have shown a high affinity of such a structure with different metals known for their potential hazardous properties.

In order to design different types of three-dimensional polymeric networks, several binders have been tested to link the CD moieties. Aromatic or aliphatic linkers have been chosen with the possibility to adjust their length and their reticulation ratio (linker per CD unit). The final goal is to optimize the design of new insoluble materials. The different synthesized materials were evaluated for their ability to extract chromium oxoanion from water solution. In

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order to correlate the extraction properties of the polymers with their chemical structural features, the most performing materials, on the base of their complexation properties, have been extensively studied with solid-state NMR. As a matter of fact, high-resolution solid-state NMR is a powerful tool to characterize the structure of polymers (Bardet, Foray, Maron, Goncalves, & Tran, 2004; Komoroski, 1986; Ngono-Ravache, Foray, & Bardet, 2001) and to study their dynamics (Bovey & Mirau, 1996; Schmidt-Rohr & Spiess, 1996; Voelkel, 1988). As we have shown in a previous work (Cadars et al., 2005), the expected interactions between the oxoanions and the polymers are weak (no covalent bonds) and do not generally induce remarkable changes in the chemical shifts on their corresponding NMR spectra. In that respect, NMR relaxation parameters have appeared as very valuable tools to probe these weak interactions since they are sensitive to the presence and the localization of the metal inside the polymers. Moreover, they are sensitive to a range of motional frequencies covering some decades. This renders the NMR technique particularly powerful since the events underwent by the polymers can be analyzed on different structural levels, starting from local molecular modifications up to overall aspects of the polymers such as its backbone mobility (McBrierty, 1997). This aspect involves mainly the dynamics of cross-polarisation, the proton spin-lattice relaxation in the rotating frame and the carbon spin-lattice relaxation, measured through their respective time constants T_{CH}, $T_{1\rho H}$ and T_{1C}. ^{1}H–^{13}C heteronuclear 2D Wideline Separation (WISE) experiments were also performed and lead to interesting conclusions concerning the dynamics of these materials.

In this contribution, we worked on dichromate or arsenate ions trapped in the different synthesized polymers (see Fig. 1). The first one was the same as in our previous study (Cadars et al., 2005) and consisted in a polymer made of per(3,6-anhydro)-α-cyclodextrin (CD) units linked together with 1,6-diisocyanatohexane (DIH). In the other polymers, the reticulation process included the use of 2,4-diisocyanatophenylene (DIP), 2,4-diisocyanatotolylene (DIT) or 1,12-diisocyanatododecane (DID) instead of 1,6-diisocyanatohexan (DIH) to bridge the per(3,6-anhydro)-α-cyclodextrin (CD) moieties. The choice of these different linkers was motivated by the hope to obtain different degrees of mobility of the polymer, a more flexible and soft polymer with DIH or DID than with DIP or DIT.

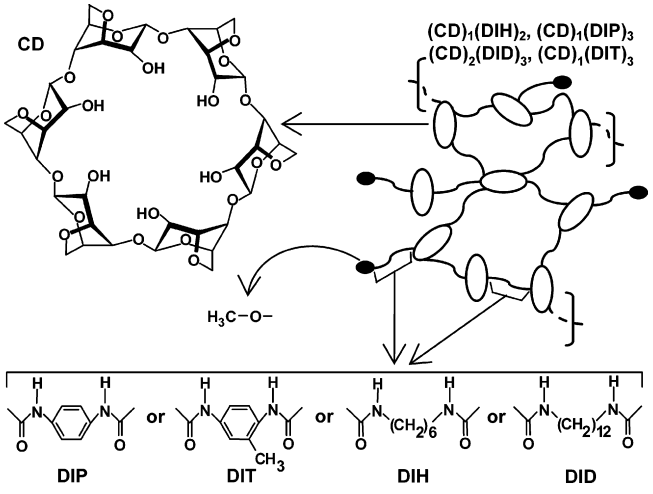

Fig. 1. Schematic representation of free $(CD)_1(DIH)_2$ and $(CD)_1(DIP)_3$ polymers. Abbreviations: CD, per(3,6-anhydro)-α-cyclodextrin; DIH, 1,6-diisocyanatohexane; DID, 1,12-diisocyanatododecane; DIP, 1,4-diisocyanatophenylene; DIT, 2,4-diisocyanatotolylene.

2. Experimental

2.1. Polymer syntheses and complex preparation

α-Cyclodextrin was a gift from Wacker (France). 1,6-Diisocyanatohexane (DIH), 1,12-diisocyanatododecane (DID), 2,4-diisocyanatophenylene (DIP), 2,4-diisocyanatotolylene (DIT) were purchased from Aldrich (USA). Reagents were used without further purification. DMF was distilled before use. Per(3,6-anhydro)-α-cyclodextrin was prepared according to Gadelle (Gadelle & Defaye, 1991).

The polymers were synthesized from per(3,6-anhydro)-α-cyclodextrin (CD) and different amounts of each diisocynate (DIH, DID, DIP and DIT). As they only differ by their relative content in both constituents, we use the following abbreviation, $(CD)_x(DIH)_y$, $(CD)_x(DID)_y$, $(CD)_x(DIP)_y$ and $(CD)_x(DIT)_y$, where x and y indicate the respective molarity of both reagents used for polymerization. The precise synthesis of the different polymers is given in Appendix A. Resulting polymers are low molecular oligomers (MW $\leqslant$ 10,000). Reactive groups were secondary alcohol. These polymers were used as starting materials to prepare their metallic complexes with chromate, dichromate or arsenate.

2.2. Elemental analyses

Elemental analyses for nitrogen, chromium and arsenic were performed by the 'Service Central de Microanalyse du CNRS' (Solaize, France). Results are given in Table 1.

2.3. Samples selected for NMR experiments

On the base of the results obtained by elemental analyses, only the polymers extracting the most of dichromate, $(CD)_1(DIH)_2$ and $(CD)_1(DIP)_3$, were studied by solid-state NMR. A schematic representation of those two polymers is shown in Fig. 1.

2.4. NMR experiments

High-resolution solid-state ^{13}C NMR spectra were recorded with a 7 mm Bruker CPMAS probehead on a Bruker AVANCE DSX 400 spectrometer operating at 100.6 MHz for the ^{13}C resonance. The 7-mm diameter

Table 1
Elemental analyses (mass %) for nitrogen, chromium and arsenic in crude, washed and complexed $(CD)_x(DIH)_y$, $(CD)_x(DIP)_y$, $(CD)_x(DID)_y$ and $(CD)_x(DIT)_y$ polymers

	Crude polymer[a]	Washed polymer[a]	$K_2Cr_2O_7$ polymer complex[a]	Na_2HAsO_4 polymer complex[a]	$K_2Cr_2O_7$ regenerated polymer[a]	Cr (mol)/CD (mol)[b]
$(CD)_1(DIH)_2$	N 5.47	N 5.12	N 4.86; Cr 1.72	N 5.67; As $\leqslant$ 500 ppm		0.40
$(CD)_1(DIH)_4$	N 8.58	N 6.84	N 6.67; Cr 0.86	N 6.67; As $<$ 0.05	N 6.53; Cr 0.02	0.24
$(CD)_2(DIP)_3$	N 3.71	N 4.78	N 4.69; Cr 1.29	N 4.93; As $\leqslant$ 500 ppm		0.30
$(CD)_1(DIP)_3$	N 8.61	N 7.51	N 7.41; Cr 1.42	N 7.62; As $\leqslant$ 200 ppm		0.32
$(CD)_2(DID)_3$	N 4.33	N 5.11	N 4.68; Cr 0.31			0.05
$(CD)_1(DID)_3$	N 5.24	N 4.63	N 4.58; Cr 0.21			0.09
$(CD)_2(DIT)_3$	N 5.73	N 4.52	N 0.46; Cr 0.46			0.12
$(CD)_1(DIT)_3$	N 8.24	N 7.70	N 6.59; Cr 1.05			0.30

Abbreviations: CD, per(3,6-anhydro)-α-cyclodextrin; DIH, 1,6-diisocyanatohexane; DID, 1,12-diisocyanatododecane; DIP, 1,4-diisocyanatophenylene; DIT, 2,4-diisocyanatotolylene.
[a] Mass %.
[b] Calculated from microanalyses results.

(340 μL) cylindrical double bearing rotors made of zirconia were filled with the dried sample (300–400 mg) and retained with Kel-F end caps. The chemical shift values were calibrated using the glycine carbonyl signal, set at 176.03 ppm relative to tetramethylsilane (TMS). The MAS spinning speed was set to 5 kHz for all the spectra. The ^1H radio-frequency field strength was set to give a 90°-pulse duration of 2.7 μs. The same field strength was used for heteronuclear dipolar decoupling. The ^{13}C radio-frequency field strength was calibrated to match the Hartman-Hahn condition during a cross-polarization (CP) experiment. The standard conditions used are 1600 transients with a contact time of 1 ms and a recycle delay of 3 s.

In the *2D WISE experiment* (Schmidt-Rohr, Clauss, & Spiess, 1992), the initial 90° ^1H excitation pulse is followed by an incremented time t_1 where the proton magnetization evolves under the influence of dipolar couplings and isotropic chemical shift. The proton magnetization is then transferred to ^{13}C using a short CP contact time (200 μs in our experiments) in order to avoid an equilibration of the proton magnetization due to spin diffusion (Hediger, Emsley, & Fischer, 1999; Suresh, Vasudevan, & Ramanathan, 2003). The MAS frequency should be set at an intermediate value, 5 kHz here, that does not affect the proton lineshape. Thus, the 2D WISE experiment correlates structural information in the ^{13}C dimension (chemical shifts) with segmental mobility in the proton dimension (lineshape). In our WISE experiments, 64 increments were collected in the indirect ^1H dimension, using TPPI for quadrature detection. For each t_1 increment, 256 transients were accumulated with a recycle time of 3 s. The spectral width in the indirect (^1H) and direct (^{13}C) dimensions was 320 and 100 kHz, respectively.

The cross-polarization (*CP*) build-up experiments (Kolodziejski & Klinowski, 2002) were performed with 21 different CP contact times, t_{CP}, ranging from 5 μs to 100 ms. The build-up of signal intensity as a function of the contact time at the different carbon chemical shift was fitted with Eq. (1) (Mehring, 1983) in order to obtain the cross-polarisation time constant, T_{CH}, and the proton spin-lattice relaxation time constant in the rotating frame, $T_{1\rho H}$:

$$M(t_{CP}) = M_0(1 - \exp(-t_{CP}/T_{CH})) * \exp(-t_{CP}/T_{1\rho H}). \quad (1)$$

$M(t_{CP})$ is the measured intensity and M_0 the initial intensity of magnetization. The value of M_0 obtained from the fit procedure is directly proportional to the number of spins, and can consequently be used for quantitative analysis.

The *carbon T_1 relaxation time constants* were obtained after the carbon magnetization has been flipped back along the magnetic field, following the method developed by Torchia (1978). A set of 15 relaxation delays between 100 μs and 120 s was measured. During this delay no heteronuclear dipolar decoupling was applied. As above, the data can be fitted and the relevant parameters extracted using the equation:

$$M(t) = M_0(\exp(-t/T_{1C})), \quad (2)$$

with $M(t)$ and M_0 defined as in Eq. (1) and T_{1C} the carbon longitudinal relaxation time constant.

For both the CP build-up and the T_{1C} relaxation measurements, no indication of a two-component phase behaviour was found. The one component fit always gave satisfying results. This point strongly indicates that the studied materials are homogeneous.

3. Results and discussion

3.1. Elemental analysis

Contrary to what has been found from the complexation tests performed on the modified cyclodextrin alone, none of the synthesized polymers has shown affinity for arsenate oxoanion.

As indicated in Table 1, eight starting polymers were synthesized to investigate the effects on the complexation

features of (i) the structure and the length of the linkers between the CD units and (ii) the ratio of CD per linkers.

In the case of the polymers containing aliphatic diisocyanates linkers, microanalysis results show that dichromate present in water is removed more efficiently by $(CD)_x(DIH)_y$ than by $(CD)_x(DID)_y$ as indicated by the results given in Table 1. The complexation properties of the materiel are not increased by the introduction of flexible linker (DID) whatever the degree of reticulation.

For the two synthesized aromatic polymers – $(CD)_x(DIP)_y$ and $(CD)_x(DIT)_y$ – the difference is not so clear. DIT differs from DIP only by the presence of a methyl group. When the ratio of reticulation is the highest, extraction properties of both polymers are similar, with about 0.3 dichromate per cyclodextrin.

As a general trend it is worthnoting that for each polymer the percentage of the dichromate species trapped increases with the degree of reticulation.

3.2. Qualitative analyses of CPMAS spectra

The spectra of $(CD)_1(DIH)_2$ and $(CD)_1(DIP)_3$ are shown in Fig. 2 and their assignment, based on our previous works and on the literature (Ashton, Ellwood, Staton, & Stoddart, 1991; Breitmaier & Bauer, 1978; Cadars et al., 2005), are reported in Table 2. The chemical shifts assigned to the CD units in the polymers are found to be exactly the same as for cyclodextrin alone. This confirms our previous results. The reaction between CD and DIH or DIP involved the hydroxyl group of CD. Whereas it induces a broadening of the resonances, no significant change in the chemical shifts of the sugar itself is observed. This is a strong indication that polymerization does not change the conformation features of CD. Additionally, the spectra

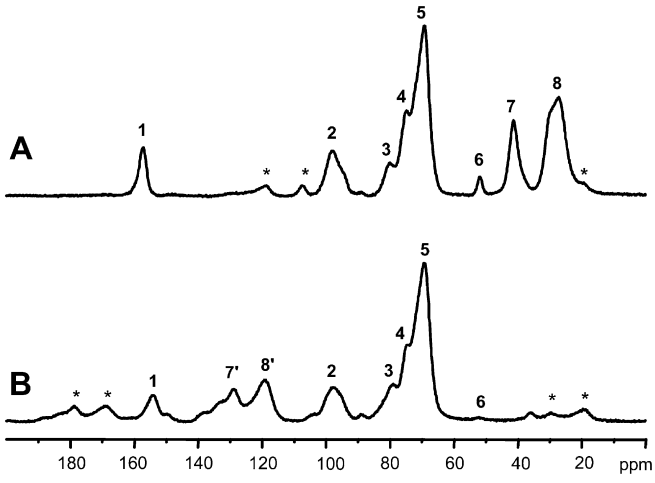

Fig. 2. ^{13}C CP/MAS high-resolution solid-state NMR spectra of free $(CD)_1(DIH)_2$ and $(CD)_1(DIP)_3$ polymers, spectrum A and B, respectively. The spectra were acquired at 5 kHz MAS with a CP contact time of 1 ms and 1600 transients were accumulated. Abbreviations: CD, per(3,6-anhydro)-α-cyclodextrin; DIH, 1,6-diisocyanatohexane; DIP, 1,4-diisocyanatophenylene.

Table 2
NMR peak assignments for $(CD)_1(DIH)_2$ and $(CD)_1(DIP)_3$ polymers

Peak number	$(CD)_1(DIH)_2$		$(CD)_1(DIP)_3$	
	^{13}C δ (ppm)	Assignment/ Carbon type	^{13}C δ (ppm)	Assignment/ Carbon type
#1	157.1	CD/C=O	154.3	CD/C=O
#2	97.7	CD/C^1H	97.6	CD/C^1H
#3	80.0	CD/CH	79.1	CD/CH
#4	74.8	CD/CH	74.4	CD/CH
#5	69.1	CD/CH, CH_2	69.3	CD/CH, CH_2
#6	52.0	DIH/OCH_3	52.1	DIP/OCH_3
#7/#7′	41.2	DIH/CH_2(NH)	128.8	DIP/C_q arom
#8/#8′	27.2	DIH/$CH_2(CH_2)$	119.0	DIP/CH arom

Abbreviations: CD, per(3,6-anhydro)-α-cyclodextrin; DIH, 1,6-diisocyanatohexane; DIP, 1,4-diisocyanatophenylene.

of both polymers $(CD)_1(DIH)_2$ and $(CD)_1(DIP)_3$ do not change at all upon complexation with dichromate, although the elemental analyses have shown significant concentrations of chromium ions in the polymers. This implies low energy interactions between the polymers and the dichromate, suggesting that the complexation does not involved any formation of covalent bound. Moreover, the above observations also exclude any oxidation of the polymer by the dichromate, since it would have lead to a paramagnetic state of chromium inducing a broadening and a shift of the NMR signals.

3.3. 2D Wideline Separation spectra

This very robust experiment leads us to record 2D maps that correlate the ^1H–^1H dipolar spectra in the indirect dimension to each resolved carbon sites in the acquisition dimension. The width of the proton lineshape is principally dominated by proton–proton homonuclear dipolar couplings (Schmidt-Rohr & Spiess, 1996) that are well known to be averaged by molecular motion. Thus, qualitative information about the mobility can be obtained from this experiment by measuring the full width at half height (FWHH) of the proton signal. The sharper the signal is, the more mobile the molecular site is. As it has been mentioned before, the CP contact time was taken sufficiently short (200 μs) to avoid spin diffusion during the 2D WISE experiment. In fact, if the contact time is too long, information about the mobility is averaged over a certain distance and all the proton lines at the different carbon sites will have the same width. Despite this precaution, the dipolar proton spectra are dominated by a superposition of several homonuclear dipolar couplings originating from the complex proton network present in organic molecules. So, there is no straightforward solution to simulate the proton lines obtained at the ^{13}C isotropic chemical shift (van Duynhoven, Kulik, Jonker, & Haverkamp, 1999). Nevertheless, qualitative analyses of the proton spectra are very useful (Qiu & Mirau, 2000).

In Fig. 3 the ^1H–^1H dipolar spectra extracted at the different ^{13}C isotropic chemical shifts given in Table 2 clearly

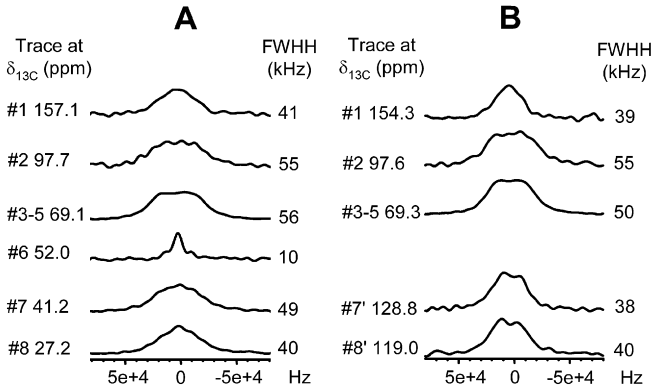

Fig. 3. ^{1}H–^{1}H dipolar spectra extracted along the proton dimension of 2D WISE experiments at the different ^{13}C isotropic chemical shifts given in Table 2 for free $(CD)_1(DIH)_2$ and $(CD)_1(DIP)_3$ polymers (A and B), respectively. Abbreviations: CD, per(3,6-anhydro)-α-cyclodextrin; DIH, 1,6-diisocyanatohexane; DIP, 1,4-diisocyanatophenylene.

illustrate the features discussed above. Considering first Fig. 3A for $(CD)_1(DIH)_2$, we see that the largest widths are observed for the CD signals #2 to #5. This result is easily explained by the rigidity and the constraints of the CD rings. The width associated to the signal #1 at 157.1 ppm of the carbonyl group CO is slightly sharper because there is no proton directly bound to this carbon. Thus, the width of the proton signal at this carbon resonance reflects the proton network surrounding the CO. The CH_3O group (signal #6) exhibits the narrowest signal. It could be surprising as strong dipolar coupling could be expected since we deal with three protons in close vicinity. As a matter of fact, the rapid rotation around the C–O bound averages the dipolar couplings between the three protons and the residual dipolar coupling is consequently decreased. Another very interesting point is the difference of 10 kHz observed for the different CH_2 belonging to the DIH chain linked to CD (signal #7 and #8). This can be explained by the higher mobility experienced by the CH_2 groups in the middle of the chain (#8) compared to the ones bound to the NCO anchored to the rigid CD (#7).

The proton spectra extracted at the ^{13}C isotropic chemical shifts for $(CD)_1(DIP)_3$ are depicted in Fig. 3B. The FWHH of traces assigned to the CD moiety and the CO are of the same order than for $(CD)_1(DIH)_2$ (signals #1 to #5). This is in good agreement with the assumption that the chemical structure of the CD moiety is the same for both polymers. The FWHH traces for the DIP linker is practically identical for the two types of aromatic carbons C and CH (signal #7 and #8). Moreover, the line shapes themselves are also identical. This point is worthwhile to mention since it means that all aromatic carbons probe an identical proton spin system with the CP contact time used (200 μs). As we expected $(CD)_1(DIP)_3$ to be more rigid than $(CD)_1(DIH)_2$, it is first of all surprising that the FWHH of the proton lines are sharper for $(CD)_1(DIP)_3$. However, the proton line width is proportional to homonuclear dipolar couplings and as we can see in Fig. 1, there are more protons in DIH than in DIP. Moreover, the mobility of the CH_2 chains in DIH induces a scaling down of the ^{1}H–^{1}H dipolar couplings leading to similar residual dipolar couplings for the CH_2 in the middle of the DIH chain and for the rigid aromatic CH in DIP. This conclusion is confirmed by the larger width measured for the proton spectra corresponding to signals #7 at 41.2 ppm assigned to the CH_2 bound to NCO in DIH, that are less mobile than the corresponding carbons localized in the middle of the chain. This observation is consistent with the different mobilities we were expecting for these polymers. Very interestingly, as seen for the 1D CPMAS experiments, complexation of the polymers with dichromate does not induce any change in the 2D WISE spectra (not shown). This strongly indicates, within the sensitivity of the technique, that the mobility of the whole polymers is not affected by the presence of the dichromate in both polymers. Indeed, a drastic change in the mobility of the polymers would induce a variation of the dipolar coupling and consequently modify the width of the proton spectra.

3.4. Carbon T_1 relaxation measurements

Carbon T_1 longitudinal relaxation is a very sensitive probe of local molecular motion for the different chemical sites resolved in the ^{13}C spectra. The molecular dynamics that influence T_1 are in the range of the MHz. T_{1C} relaxation times are interesting since spin diffusion between ^{13}C nuclei is a negligible process due to the low natural abundance of the ^{13}C isotope. Consequently, the dynamic information contained in T_1 values is obtained at a localized molecular level, in contrast to the proton line widths measured previously, which reflect the averaged dynamics over a larger molecular domain.

T_{1C} experiments were performed on $(CD)_1(DIP)_3$ and $(CD)_1(DIH)_2$, respectively. The T_{1C} time constants for the different resonances were obtained using Eq. (2) by fitting the extracted experimental intensities from spectra and are displayed in Fig. 4. For all resonances, the relaxation behaviour was found to be mono-exponential. As a general trend, the T_{1C} relaxation time constants of starting $(CD)_1(DIP)_3$ are found to be longer than for corresponding $(CD)_1(DIH)_2$ confirming the higher mobility of $(CD)_1(DIH)_2$. Although the T_{1C} values of CD sites in $(CD)_1(DIH)_2$ are shorter than the corresponding constant times in $(CD)_1(DIP)_3$, their relative behaviour are found to be similar. For $(CD)_1(DIP)_3$ the T_{1C} relaxation time constants of all resolved ^{13}C-sites are in the same range for both CD and DIP (except for the CO, not shown), which suggests a common relaxation mechanism for all sites. The T_{1C} values are more contrasted in $(CD)_1(DIH)_2$, where significantly longer times are found for the carbons of the CD unit. This undoubtedly indicates the greater mobility, in the MHz regime, of DIH chain compared to CD or DIP.

For $(CD)_1(DIP)_3$, we observe that the T_{1C} relaxation time constants globally decrease for all resolved sites when dichromate is introduced in the polymer. In complexed

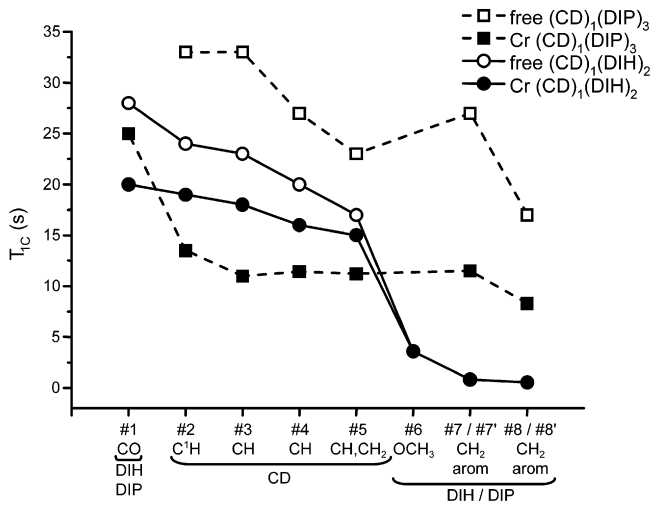

Fig. 4. Carbon longitudinal relaxation time constants T_{1C} of free and complexed $(CD)_1(DIP)_3$ and $(CD)_1(DIH)_2$. T_{1C} data points are connected by straight lines for a better reading of the figure. The isotropic chemical shift for the different sites can be found in Table 2. Abbreviations: CD, per(3,6-anhydro)-α-cyclodextrin; DIH, 1,6-diisocyanatohexane; DIP, 1,4-diisocyanatophenylene.

$(CD)_1(DIP)_3$ all T_{1C} become very similar with values around 10 s, except for the carbonyl resonance with T_{1C} at 25 s (nevertheless, in the starting polymer the carbonyl T_{1C} was too long to be measure with the experimental conditions used). This general decrease to an almost identical value is entirely attributed to the contribution of quadrupolar relaxation due to the presence of the Chromium ($I = 3/2$), which mask the specific contribution of mobility for the different sites. An increase of mobility was excluded by the 2D WISE experiments and will be confirmed latter with the measurement of T_{CH}. This overall and systematic decrease seems to indicate that the complexation of dichromate is not localized, but happens both in the cavity of the CD and in the vicinity of the aromatic rings. Interactions between dichromate and the electronic cloud of the phenyl rings, like in sandwich complexes, can be considered and can explain the presence of the dichromate near the DIP linkers.

The behaviour of the dichromate $(CD)_1(DIH)_2$ complex is completely different. Only the T_{1C} of the CD moiety are affected by the presence of the dichromate, which causes the decrease of these specific relaxation time constants. The T_{1C} values of DIH carbon sites are insensitive to complexation except for the CO group, which is explained by its close vicinity to the cavity of the CD unit. We can conclude that in the polymer $(CD)_1(DIH)_2$ the dichromate is exclusively complexed inside the CD cavity of the polymer $(CD)_1(DIH)_2$.

The more pronounced impact of dichromate complexation on the T_{1C} values of $(CD)_1(DIP)_3$ is attributed to the fact that the dichromate lies in the whole polymer contrary to the $(CD)_1(DIH)_2$ case where it is localized only in the CD cavities. In this way, the CD moiety of the polymer see more dichromate in $(CD)_1(DIP)_3$ than in $(CD)_1(DIH)_2$ and thus the T_{1C} are more affected for the $(CD)_1(DIP)_3$ polymer.

3.5. Variable contact time CPMAS experiments

Cross-polarisation time constants T_{CH}, and proton spin-lattice relaxation times in the rotating frame $T_{1\rho H}$, were computed from the experimental magnetization build-up curves using Eq. (1) and are presented in Figs. 5 and 6, respectively. As for the carbon T_1 experiments, all the curves could be fitted with a one phase-component model. It clearly indicates that the synthesized polymers are and remain homogeneous upon complexation with dichromate, indicating that the metal is very well spread inside the polymers.

In Fig. 5, the cross-polarisation time constants, T_{CH}, for the different polymers are displayed. For both polymers, the T_{CH} time constants are globally not affected by the metal complexation. The enlargement in Fig. 5 represents the CD region and shows that the variations of T_{CH} are within the uncertainty of the experiments for both polymers and independent of the complexation. This indicates that the mobility is not affected by the presence of the dichromate, since homonuclear and heteronuclear dipolar couplings (which determine mainly T_{CH} values) remain globally the same. This observation is in agreement with the 2D WISE and the T_{1C} experiments, from which we concluded that there is no modification of the mobility when the dichromate is introduced in the polymer. Moreover, the fact that there are no strong variations in T_{CH} for the polymer with and without dichromate confirms one more time that no covalent bonds are formed when the metal is introduced.

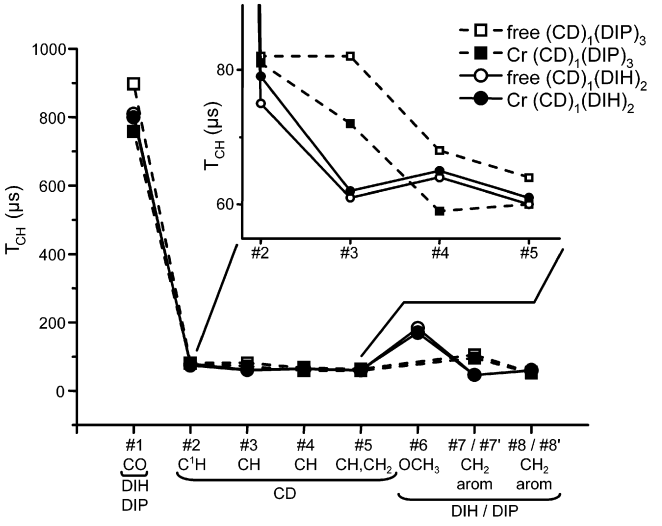

Fig. 5. Cross-polarisation time constants T_{CH} of free and complexed $(CD)_1(DIP)_3$ and $(CD)_1(DIH)_2$ obtained from a CP build-up experiment. T_{CH} data points are connected by straight lines for a better reading of the figure. The isotropic chemical shift for the different sites can be found in Table 2. Abbreviations: CD, per(3,6-anhydro)-α-cyclodextrin; DIH, 1,6-diisocyanatohexane; DIP, 1,4-diisocyanatophenylene.

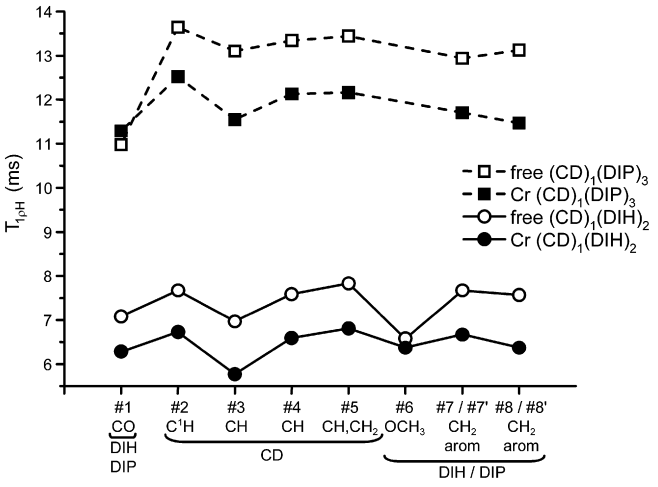

Fig. 6. Proton spin-lattice relaxation time constants in the rotating frame $T_{1\rho H}$ of free and complexed $(CD)_1(DIP)_3$ and $(CD)_1(DIH)_2$ obtained from a CP build-up experiment. $T_{1\rho H}$ data points are connected by straight lines for a better reading of the figure. The isotropic chemical shift for the different sites can be found in Table 2. Abbreviations: CD, per(3,6-anhydro)-α-cyclodextrin; DIH, 1,6-diisocyanatohexane; DIP, 1,4-diisocyanatophenylene.

Fig. 6 shows the results obtained for the proton spin-lattice relaxation time constants in the rotating frame, $T_{1\rho H}$. This relaxation is characteristic of motion in the regime of the kHz (Stejskal, Schaefer, & Steger, 1979). In contrary to carbon T_1 relaxation time constants which are very local probes of mobility, proton $T_{1\rho H}$ time constants are averaged by spin diffusion over a certain distance (a few nm). With this parameter we can therefore have some insight in the homogeneity of a compound within the volume (of some nm^3) explored. If the material is homogeneous, all $T_{1\rho H}$ values are similar and a unique proton spin bath can be considered for the whole sample. Inversely, if there are two different domains in the compounds, for example, the $T_{1\rho H}$ values will be separated in two groups, providing the domain dimensions are larger than the spatial averaging by spin diffusion. In such a case, two distinct proton spin baths are observed.

As we can see in Fig. 6, the measured $T_{1\rho H}$ values are homogeneous for the free polymers as well as for the complexed ones. In every case a unique proton spin bath is detected, and the homogeneous slow motions found with the $T_{1\rho H}$ experiments are not affected, as expected, by the motions in the MHz frequency range revealed by the T_{1C} experiments. A very interesting point is that the $T_{1\rho H}$ time constants of each carbon sites in the polymer are sensitive to the presence of dichromate. If this can be obvious for $(CD)_1(DIP)_3$ since the metal is present everywhere in the polymer, it is not the case for $(CD)_1(DIH)_2$ where dichromate is only located in the CD cavities. It seems that the scale of the spatial averaging by spin diffusion is larger than the monomer unit. Using $T_{1\rho H}$ relaxation time constants, we can therefore distinguish the different starting polymers as well as the complexed states, but we loose the information about the precise location of the dichromate in the polymer.

As discussed for the T_{1C} measurements, the decrease in the $T_{1\rho H}$ values in our systems is entirely attributed to the interaction with the quadrupolar moment of the Chromium and not to an increase of the mobility, which was not detected through the T_{CH} values and 2D WISE experiments.

4. Conclusions

The question addressed in this paper was to obtain valuable information about the molecular dynamics in different polymers and about the localization of a metal complex in two different polymers. High frequency dynamics in the MHz range was explored with T_{1C} measurements whereas low frequency motions were probed with $T_{1\rho H}$ time constants. The results obtained are in agreement with those obtained from 2D Wideline Separation experiments.

We have shown that the two polymers made of per(3,6-anhydro)-α-cyclodextrins (CD) with 1,6-diisocyanatohexan (DIH) or 1,4-diisocyanatophenylen (DIP) used to bridge the macrocycles, $(CD)_1(DIH)_2$ and $(CD)_1(DIP)_3$, respectively, exhibit different mobility as expected. The T_{1C} experiments revealed that $(CD)_1(DIH)_2$ is more mobile than $(CD)_1(DIP)_3$ whose T_{1C} are longer. This difference of mobility was attributed to the presence of the CH_2 chain (DIH) in the $(CD)_1(DIH)_2$ polymer. The mobility of the DIH spacer was confirmed by shorter T_{1C} values than for CD carbon sites in the polymer which is also consistent with the results obtained from 2D WISE experiments. T_{1C} relaxation time constants also allowed precise localization of the dichromate in the polymer. Indeed, as all T_{1C} where affected in $(CD)_1(DIP)_3$, we concluded that the dichromate is present in the whole polymer. In contrary, in $(CD)_1(DIH)_2$, only T_{1C} of CD carbon resonances were modified upon complexation indicating exclusive location of the dichromate inside the CD cavities. This point is confirmed by the more pronounced variation of the T_{1C} values for $(CD)_1(DIP)_3$ than for $(CD)_1(DIH)_2$ when the dichromate is introduced in the polymer.

The $T_{1\rho H}$ values extracted from CP build-up experiment are characteristic of slow motions in the kHz range. With this parameter we have shown that the mobility is homogeneous over the entire polymers and this homogeneity is not altered by the presence of the dichromate, which only decrease the overall relaxation time. Very different values of $T_{1\rho H}$ were found for both polymers as well as when the metal was incorporated. However, information about precise dichromate localization is lost.

The decrease of the T_{1C} and $T_{1\rho H}$ values after complexation of the polymer with dichromate was attributed to interactions with the quadrupolar moment of the

Chromium and not to an increase of the mobility. This explanation was supported by the T_{CH} time constants which are insensitive to complexation and by the 2D WISE experiments were the proton lineshape are not modified by the presence of the dichromate in the polymer.

Appendix A

Table A1. Preparations of $(CD)_x(DIH)_y$ polymers and their complexes

$x/y = 1/2$ (mol/mol)	Polymerisation	CD (2.5 g) DMF (5 mL) DIH (0.93 mL) 90°, 15 h, magnetic stirring. Then MeOH (15 mL) was added and after 1 h DMF was removed. The solid residue was dispersed in water (50 mL) and recuperated by centrifugation and dried (3.21 g)
	Reference polymer	Polymer (0.7 g) was dispersed in water (20 mL – 1 h) and centrifuged (4 times) then dried (0.655 g)
	Complexation	Polymer (0.7 g) was dispersed in a solution of $K_2Cr_2O_7$ (60 mg) in water (20 mL) for 15 h. The sample was centrifuged. Solid material was washed with water (20 mL – 1 h) and centrifuged (3 times) and dried (0.632 g)
$x/y = 1/4$ (mol/mol)	Polymerisation	Same as $x/y = 1/2$ but DIH (1.80 mL) and solid residue recuperated by centrifugation and dried (2.52 g–2.22)
	Reference polymer	Polymer (0.7 g) was dispersed in water (20 mL – 1 h) and centrifuged (4 times) and dried (0.653 g)
	Complexation	Same as $x/y = 1/2$ but solid material dried (0.625 g)

Abbreviations: CD, per(3,6-anhydro)-α-cyclodextrin; DIH, 1,6-diisocyanatohexane.

Table A2. Preparations of $(CD)_x(DID)_y$ polymers and their complexes

$x/y = 2/3$ (mol/mol)	Polymerisation	CD (1.730 g) DMF (8 mL) DID (0.8 mL) 90°, 15 h, magnetic stirring. Then MeOH (10 mL) was added and after 1 h DMF was removed under reduced pressure. The solid residue was dispersed in water (50 mL), recuperated by centrifugation and dried at room temperature (1.944 g)
	Reference polymer	Polymer (0.7 g) was dispersed in water (20 mL – 1 h) and centrifuged (4 times) then dried (0.644 g)
	Complexation	Polymer (0.7 g) was dispersed in a solution of $K_2Cr_2O_7$ (60 mg) in water (20 mL) for 15 h. The sample was centrifuged. Solid material was washed with water (20 mL – 1 h) and centrifuged (3 times) and dried (0.614 g)
$x/y = 1/3$ (mol/mol)	Polymerisation	Same as $x/y = 2/3$ but DID (1.6 mL) and solid residue was recuperated by centrifugation and dried at room temperature (2.990 g)
	Reference polymer	Polymer (0.7 g) was dispersed in water (20 mL – 1 h) and centrifuged (4 times) then dried (0.64 g)
	Complexation	Same as $x/y = 2/3$ but solid material dried (0.65 g)

Abbreviations: CD, per(3,6-anhydro)-α-cyclodextrin; DID, 1,12-diisocyanatododecane.

Table A3. Preparations of $(CD)_x(DIP)_y$ polymers and their complexes

$x/y = 2/3$ (mol/mol)	Polymerisation	CD (1.73 g) DMF (4 mL) DIP (0.480 g) 90°, 15 h, magnetic stirring. Then MeOH (10 mL) was added and after 1 h DMF was removed under reduced pressure. The solid residue was dispersed in water (50 mL), recuperated by centrifugation and dried at room temperature (1.97 g)
	Reference polymer	Polymer (0.6 g) was dispersed in water (20 mL – 1 h) and centrifuged (4 times) then dried (0.290 g)
	Complexation	Polymer (0.6 g) was dispersed in a solution of $K_2Cr_2O_7$ (294 mg) in water (20 mL) for 15 h. The sample was centrifuged. Solid material was washed with water (20 mL – 1 h) and centrifuged (3 times) and dried (0.370 g)
	Complexation	Polymer (0.7 g) was dispersed in a solution of Na_2HAsO_4 (216 mg) in water (20 mL) for 15 h. The sample was centrifuged. Solid material was washed with water (20 mL – 1 h) and centrifuged (3 times) and dried (0.330 g)
$x/y = 1/3$ (mol/mol)	Polymerisation	Same as $x/y = 2/3$ but DMF (8 mL) DIP (0.960 g) and solid residue recuperated by centrifugation and dried at room temperature (1.63 g)
	Reference polymer	Polymer (0.6 g) was dispersed in water (20 mL – 1 h) and centrifuged (4 times) then dried (0.480 g)
	Complexation	Same as $x/y = 2/3$ but solid material dried (0.580 g)
	Complexation	Same as $x/y = 2/3$ but solid material dried (0.510 g)

Abbreviations: CD, per(3,6-anhydro)-α-cyclodextrin; DIP, 1,4-diisocyanatophenylene.

Table A4. Preparations of $(CD)_x(DIT)_y$ polymers and their complexes

$x/y = 2/3$ (mol/mol)	Polymerisation	CD (1.730 g) DMF (8 mL) DIT (522 mg) 90°, 15 h, magnetic stirring. Then MeOH (10 mL) was added and after 1 h DMF was removed under reduced pressure. The solid residue was dispersed in water (50 mL), recuperated by centrifugation and dried at room temperature (2.161 g)
	Reference polymer	Polymer (0.7 g) was dispersed in water (20 mL – 1 h) and centrifuged (4 times) then dried (0.585 g)
	Complexation	Polymer (0.7 g) was dispersed in a solution of $K_2Cr_2O_7$ (60 mg) in water (20 mL) for 15 h. The sample was centrifuged. Solid material was washed with water (20 mL – 1 h) and centrifuged (3 times) and dried (0.586 g)
$x/y = 1/3$ (mol/mol)	Polymerisation	Same as $x/y = 2/3$ but DIT (1.044 g) and solid residue recuperated by centrifugation and dried at room temperature (2.793 g)
	Reference polymer	Polymer (0.7 g) was dispersed in water (20 mL – 1 h) and centrifuged (4 times) then dried (0.603 g)
	Complexation	Same as $x/y = 2/3$ but solid material dried (0.591 g)

Abbreviations: CD, per(3,6-anhydro)-α-cyclodextrin; DIT, 2,4-diisocyanatotolylene.

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