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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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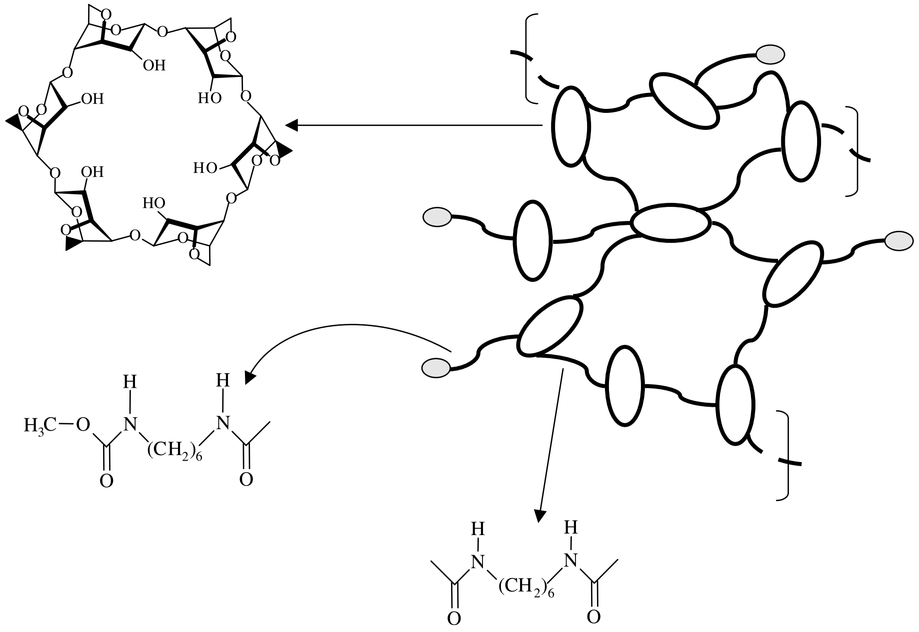

Fig. 1. Schematic representation of the starting polymer $(CD)_x(DIH)_y$. Abbreviations: CD, 3,6-anhydro-α-cyclodextrin; DIH, 1,6-diisocyanato-hexan.

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

Table 1
Preparations of 3,6-anhydro-α-cyclodextrin polymers and of their complexes

CD_x/DIH_y (mol/mol)			DIH_x/CD_y (mol/mol)	Cr/CD (mol/mol)	H_2O (mol/mol)
1/2	Polymerisation conditions	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 collected by centrifugation and dried (3.21 g)	2.5		
	Reference polymer	Polymer (0.7 g) was dispersed in water (20 mL–1 h) and centrifuged (4 times) then dried (0.655 g)	2.08	–	
	Complexation conditions	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)	2.27–2.22	0.41–0.39	
1/4	Polymerisation conditions	CD (2.5 g) DMF (5 mL) DIH (1.80 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 collected by centrifugation and dried (2.52 g–2.22)	4.3		
	Reference polymer	Polymer (0.7 g) was dispersed in water (20 mL–1 h) and centrifuged (4 times) and dried (0.653 g)	3.54	–	4–5
	Complexation Conditions	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 (0.625 g)	3.40	0.24	1–1.5
		Polymer (0.7 g) was dispersed in a solution of K_2CrO_4 (46 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 (0.658 g)	3.48	0.15	1.5–2

Abbreviation: CD, per(3,6-anhydro)-α-cyclodextrin; DIH, 1,6-diisocyanato-hexan. MW≅1430 for measurement of water.

polymers as starting materials, their complexes with chromate and dichromate were prepared. The preparation conditions of the different starting polymers and of their complexes are summarised in Table 1.

2.2. Regeneration of starting polymers

Sodium sulphite reduces potassium dichromate in acidic medium according to the following equation:

$$3SO_3^{2-} + Cr_2O_7^{2-} + 8H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + 4H_2O$$

The orange chromic acid can be reduced to the green chromic ion Cr^{3+} It was possible to obtain this reduction in acetic acid solutions (Gadelle, 2002). These conditions were consistent with the stability of our synthetic polymers. The chromium complex polymer dispersed in a solution of acetic acid (500 mg, 50 ml 10%) was treated with sodium sulphite (200 mg). After centrifugation an elemental analysis for chromium was performed.

2.3. Elemental analyses

Elemental analyses for nitrogen and chromium were performed by the 'Service Central de Microanalyse du CNRS' (Solaize, France). The following results have been obtained:

$(CD)_1(DIH)_2$

Crude polymer, N 5.47. Washed polymer, N 5.16–5.08. $K_2Cr_2O_7$ polymer complex, N 4.86; Cr 1.72.

$(CD)_1(DIH)_4$

Crude polymer, N 8.58. Washed polymer, N 6.84. $K_2Cr_2O_7$ polymer complex, N 6.67; Cr 0.87–0.86. $K_2Cr_2O_7$ regenerated polymer complex, N 6.53; Cr 0.02. K_2CrO_4 polymer complex, N 6.74; Cr 0.55.

2.4. NMR experiments

High-resolution solid-state ^{13}C NMR spectra were mainly recorded on a BRUKER AVANCE DSX 400 MHz spectrometer operating at 100.6 MHz for ^{13}C, using the combination of cross-polarisation, high-power proton decoupling and magic angle spinning (CP/MAS) methods. The spinning speed was set in the range of 4000 Hz. The ^1H radio-frequency field strength was set to give a 90°-pulse duration around 2.7 μs; the same value was used for the dipolar decoupling process. The ^{13}C radio frequency field strength was obtained by matching the Hartman–Hahn condition. Recording 1024 transients with contact time and recycle delay, respectively of 1 ms and 3s represented standard conditions. The chemical shift values were obtained via the glycine carbonyl signal, set at 176.03 ppm relative to tetramethylsilane (TMS). In order to record spinning-sideband-free spectra the TOSS experiment was used (Dixon, Schaefer, Sefcik, Stejskal, & McKay, 1982). The dynamic study of the carbon magnetisation build-up under CP conditions was performed at 50.3 MHz on a BRUKER MSL 200 spectrometer. From these experiments, $T_{1\rho H}$ and T_{CH} were computed by using simplex fitting program (SIMFIT) provided by Bruker. Measurements of T_{1C} spin–lattice relaxation times were performed according to the method developed by Torchia (1984) that is based on proton-enhanced spectra. Interrupted decoupling experiments were performed by intervalling in the CP experiment a 40 μs delay with a zero field strength before the acquisition period (Opella & Frey, 1979). The amplitude of the ^{13}C NMR signal in a CP experiment is dependent on the contact times (Pines, Gibby, & Waugh, 1973). In order to get quantitative data, dynamic studies of the carbon magnetization build-up were performed by varying the contact values from 10 μs to 20 ms and exploited as described in the experimental section of one of our preceding article (Bardet, Foray, Maron, Goncalvez, & Tran, 2004). The main point to be reminded is that these studies allow the integrals from different NMR signals to be corrected. Therefore, the corrected integrals are comparable.

3. Results and discussion

3.1. Qualitative analyses of the NMR spectra

The spectra B and C of both starting polymers $(CD)_1(DIH)_2$ and $(CD)_1(DIH)_4$ are shown in Fig. 2. For $(CD)_1(DIH)_4$ polymer, the spectra D and E of its complexes with chromate and dichromate are also given in Fig. 2. The spectrum A recalls the NMR feature of the starting CD.

As a general observation, the spectra of the starting polymers and of their complexes appear to be very similar. They exhibit distinct regions easily assigned to CD and to DIH. The region assigned to CD is found between 60 and 105 ppm, while the high-field region is attributed to the different carbons C-1, C-2 and C-3 belonging to the DIH. The carbon of its carbonyl appears at 160 ppm as expected. These assignments are based on data reported in literature (Breitmaier & Bauer, 1978). Qualitatively, the only difference in this series of spectra is the occurrence of a signal at 52 ppm in the starting polymers $(CD)_1(DIH)_4$ and its corresponding complexes with chromate or dichromate. On the basis of the synthesis routes that were employed, this signal can be unambiguously assigned to the carbon of methoxy group. It originates from the reaction of methanol on the hydroxyl groups. These hydroxyls are formed, in the polymer preparation, by the reaction of water on the unreacted DIH end groups. As this reaction is known to be quantitative, the integration of the NMR methoxy signal should allow the proportion of free DIH end groups to be estimated.

It is worth noting that in the spectrum A (Fig. 1) of the starting CD, the signal assigned to C-1 is made of three sharp signals with comparable intensities. It clearly indicates a three-fold symmetry in the crystalline structure. The decrease in the NMR signal resolution observed on the spectra B and C (Fig. 2) for both starting polymers $(CD)_1(DIH)_2$ and $(CD)_1(DIH)_4$ is certainly due to the dispersion in chemical shifts arising from a statistical spreading of the bounding of DIH on the 3,6-anhydro-α-cyclodextrin. It leads to less well-defined chemical structures for the different carbons of the CD.

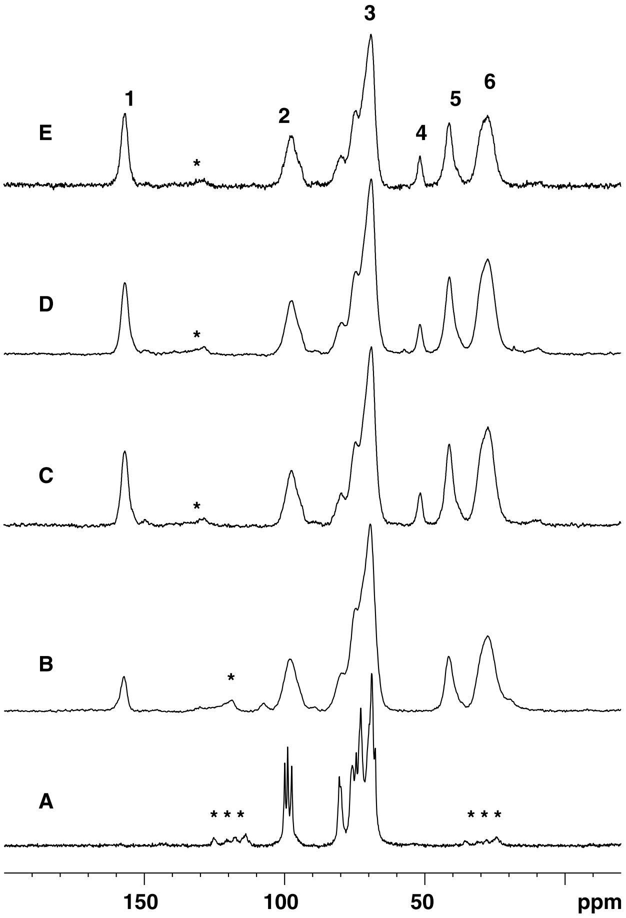

Fig. 2. 100 MHz CP/MAS ^{13}C high-resolution solid state NMR spectra of the 3,6-anhydro-α-cyclodextrin based polymers and of their chromium complexes: (A) 3,6-anhydro-α-cyclodextrin alone, (B) $(CD)_1(DIH)_2$, (C) $(CD)_1(DIH)_4$, (D) chromate complex of $(CD)_1(DIH)_4$ and (E) dichromate complex of $(CD)_1(DIH)_4$. Abbreviations: CD, 3,6-anhydro-α-cyclodextrin; DIH, 1,6-diisocyanato-hexan.

On the one hand, as the reaction occurs between the DIH and the different hydroxyls of the CD, it is not surprising that the chemical shifts of the sugar moiety itself in the polymers do not differ from those of the CD alone. On the other hand, both X-ray studies on similar cyclodextrins and molecular dynamic calculations that we performed on the CD are consistent and both showed that the hydroxyls are oriented preferentially towards the cavity of the macrocycle. Therefore, the fact that we do not observe any significant changes in the chemical shifts of the different carbons of the CD, clearly indicates that the general conformation of the CD is unchanged when going from the isolated macrocycle towards its polymeric forms. Only a general broadening of the NMR lines is observed. Nevertheless, even if it indicates that theses materials become less ordered than the starting CD, their linewidths in the range of 200 Hz remain rather narrow for this type of polymers. It has to be remembered that these materials still contain about 6% of water that is known to play a strong plasticiser effect on the polymer by releasing the molecular constraints within the polymers. This phenomenon is well known in sugar polymers and their derivatives (Bardet, Rousseau, & Vincendon, 1993). In the present case after drying the starting polymers for 3 days at 100 °C, no broadening of the NMR lines within the spectra could be observed (spectra not reported herein). Such a very simple experiment rules out the predominant role of water for the reasons indicated above. It shows that the conformational domains of these polymers remain rather well defined and narrow**.** It indicates that these materials are merely ordered materials. The fact that their structural properties are not sensitive to water content may be an important feature for their further applications.

The spectra also show spinning sidebands that have to be carefully identified in order not to be assigned to isotropic chemical shifts. Indeed, due to the strong chemical shift anisotropy of the carbonyl carbons the magic angle spinning in the range of 3500–4000 Hz is not high enough to completely average this interaction and consequently spinning side bands, indicated by star symbols in the spectra, appear. These spinning side bands are unambiguously identified either with the TOSS experiment or by recording spectra at different spinning rates (Dixon, Schaefer, Sefcik, Stejskal, & McKay, 1982).

3.2. NMR analyses of the chromium polymer complexes

Very interestingly as mentioned previously, the complexation with chromate or dichromate has not significantly modified the spectral features of both polymers. For instance, on the spectra C–E (Fig. 2) it is practically not possible to despite differences in the spectral region assigned to the CD moiety between the starting polymer $(CD)_1(DIH)_4$, spectrum C, and its two complexes. Note that the amount of oxoanions that have been included in the polymers appears to be high as reported in Table 2. It is important to recall that these materials were stirred efficiently against water in order to remove all the excess of salts that could weakly interact with the polymers.

Several important conclusions can be drawn from the above observations. The diamagnetic state of the oxoanions is not affected since no spectral property, which could be due to paramagnetism, is noticeable on the spectra. For instance, such interactions, if they were present, should have broadened the NMR lines and they should have led to important changes in the chemical shifts. As the oxidant properties of the chromate and dichromate are well established, this result is interesting since it demonstrates that the CD moieties of the polymers have not been oxidised by these metals. The CD based polymers appear to be suitable material to bind and retain chromate and dichromate from solutions in their unmodified native form. It is an important result, for the industrial use of these materials. On the contrary, all the tests we performed in the laboratory with polymers made of more mobile sugars such as unbridged cyclodextrin or inositol showed that they were readily oxidised by these cations and therefore such polymers could not be retained as potential materials for complexation of chromate or dichromate.

Table 2
Structural parameters of $(CD)_1(DIH)_x$ polymers and of their chromium complexes obtained from the solid-state ^{13}C NMR spectra

Polymer	$(CD)_1(DIH)_2$		$(CD)_1(DIH)_4$		
	Starting	Dichromate (0.39–0.41)[a]	Starting	Chromate (0.15)[a]	Dichromate (0.24)[a]
r	1.96	1.90	3.78	3.72	3.8
n	0	0	0.432	0.45	0.439
t	3.9	3.8	5.9	5.8	5.94

r is the molar ratio of 1,6-diisocyanato-hexan versus 3,6-anhydro-α-cyclodextrin, n is the ratio of free diisocyanate end group per diisocyanato-hexan chain. t is the number of substituent per cyclodextrin macrocycle, CD.

[a] Chromium concentrations, expressed as Cr/CD (mol/mol), they are calculated from the elemental analyses.

3.3. Quantitative analyses

The complete assignment of the spectra performed above has shown that, on the one hand the signals of CD and those assigned to the DIH do not overlap and on the other hand the methoxy signal is the signature of unbranched DIH. Consequently, quantitative analyses on these materials can be carried out and the three structural parameters were defined and calculated as followed:

— Firstly, the molar ratio r of DIH versus CD, calculated as

$$r = [(I_{41})/2]/[(I_{69})/30]$$

where $I_{41}$and I_{69} are the integral of the signals at 41 and 69 ppm, respectively.
They are divided by their corresponding number of carbons, respectively, 2 and 30.

— Secondly, the ratio, n, of free DIH end group per aliphatic chain. It corresponds to the amount of methoxy per aliphatic chain. Therefore, n is calculated as

$$n = [(I_{52})]/[(I_{156})/2]$$

where I_{52} and I_{156} are the integrals of the signals at 52 and 156 ppm, respectively. I_{156} is divided by two, the corresponding number of carbons.

— Thirdly, the crosslinking factor, t, of the polymer can be calculated from the previous n and r ratio, using the following formula:

$$t = 2r - nr$$

The results found for the two types of $(CD)_1(DIH)_y$ polymers and their metallic complexes are given in Table 3. Some interesting points may be highlighted.

For the starting polymers, the number of DIH per CD found by NMR corresponds to that expected from the synthesis protocol, respectively, 2 and 4. The data found for the complexes are identical to those of the starting polymers.

It is another clear indication that both polymers, $(CD)_1(DIH)_2$ and $(CD)_1(DIH)_4$ have not undergone any chemical modification during their complexation with chromate or dichromate.

As far as the number of substituents per cyclodextrin is concerned, the quantitative analyses demonstrate that by increasing the amount of DIH the amounts of covalent bonds, between the CD and the aliphatic chain, is increased from 4 to around 6. It indicates that with the synthesis route we used, the maximum theoretical crosslinking factor has been reached. A complete study on the effects of the crosslinking factor, *t*, on the amounts of chromate or dichromate that can be bound by these polymers has not been performed in the present work. However, from Table 2, it clearly appears that the amounts of chromium strongly decrease as the polymers become more reticulated. This trend can be easily explained by a drop in the accessibility of the bounding sites of the polymers. In order to synthesise crosslinked polymers with the highest binding properties, the possibility of adjusting and measuring their crosslinking factors is a undoubtedly a crucial point for the elaboration of suitable material with the expected properties.

3.4. Molecular dynamic studies

Values of cross-polarisation times, T_{CH}, proton spin–lattice relaxation times in the rotating frame, $T_{1\rho H}$ and carbon spin–lattice relaxation times T_{1C} are reported in Table 3. In a first approximation, T_{CH} is mostly dependent on the proton–carbon dipolar interactions; therefore, local motions can affect it. Its value decreases as the dipolar interactions increase. Such is the case, when the number of protons either bound to a carbon or in its surrounding becomes greater. This general rule does not stand for the CH_3 groups since its internal motion leads to a partial averaging of dipolar interactions. Values of T_{CH} found for carbons of both aliphatic and cyclodextrin are fully consistent with this general expected behaviour and present increasing values in the series CH_2, CH, CH_3 and quaternary carbons.

If we compare the signals at 41 and 28 ppm that are both assigned to CH_2, a significant difference appears between their T_{CH} values since a higher value is found for the signal at 28 ppm. It indicates that the CH_2 groups at 28 ppm are more mobile than those at 41 ppm that are assigned to methine directly bound to carbonyls. It is consistent with the fact that they are localised in the middle of the isocyanate chain. Moreover, two points have to be underlined. The T_{CH} of methoxy group found for the dichromate polymer is shorter than the values found for the dichromate polymer or the reference polymer. It can indicate a lower mobility of the methoxy group in the dichromate polymer than in the two other materials. An interesting point has also to be noted, it is the fact that the T_{CH} associated with the carbonyl in the chromate polymer appears to be longer than those of the control and of the dichromate polymers. For such a functional group, only a drastic decrease in the number of protons in its surrounding, arising from water molecules, can explain such an observation.

The proton $T_{1\rho H}$ values in solids usually represent an average value of the relaxation behaviour over the ensemble of protons. This is the case because of the efficient spin diffusion due to the strong dipolar coupling between the protons. It allows the homogeneity of a material at a molecular level to be estimated.

From the table, it clearly appears that the chromate polymer present an homogeneous behaviour as far $T_{1\rho H}$ is concerned since the same value is found for all the carbons, except for the methoxy group, for which its local motion certainly breaks the efficiency of proton spin diffusion.

On the contrary, the behaviour of the dichromate polymer as far its dynamic is concerned is very similar to the reference polymer. It is still possible to distinguish a specific behaviour for the cyclodextrin and for the isocyanate chain.

Table 3
Peak assignments and relaxation parameters (T_{CH}, $T_{1\rho H}$, T_{1C}) of the starting $(CD)_1(DIH)_4$ and of its chromium chromate and dichromate complexes

Region or peak number		1	2	3	4	5	6
Chemical shift (ppm)		156 ppm	98 ppm	80-60 ppm	52 ppm	41 ppm	28 ppm
Assignment		CD	CD	CD	DIH	DIH	DIH
Carbon type		C	CH	CH, CH2	OCH3	CH2	CH2
T_{CH} (μs)	Control	525	131	109.8	179	88.2	97.5
	Chromate	762	123	101	172	77.3	89.5
	Dichromate	527	126	118.5	145.4	83.5	103.8
$T_{1\rho H}$ (μs)	Control	9116	7042	7297	8340	5849	5827
	Chromate	5064	5380	5296	6815	5103	4892
	Dichromate	9165	7633	7704	10012	6579	6050
T_{1C} (ms)	Control	13020	13210	11120	3570	657	413
	Chromate	17570	14990	12560	3150	772	420
	Dichromate	17260	15530	12660	5140	974	530

Abbreviations: CD, 3,6-anhydro-α-cyclodextrin; DIH, 1,6-diisocyanato-hexan; control stands for the starting polymer $(CD)_1(DIH)_4$.

From these data, the interpretation we can propose is the following; as the amounts of chromate and dichromate that are retained are large, the fact that we have not observed any change for the $T_{1\rho H}$ value for dichromate, is a clear indication that these are localised inside the cavities of the cyclodextrin. On the other hand, the chromate has to be localised outside the cavities of modified cyclodextrin.

An interesting point to exploit is the fact that the T_{CH} associated with the carbonyl in the chromate polymer is longer than those of the control and the dichromate polymers. This observation allows the chromate to be localised in close interactions with the oxygen of carbonyl whereas water molecules in the starting polymer and in the dichromate occupy this chemical site.

4. Conclusion

The results we obtained in the present work demonstrate the usefulness of solid-state ^{13}C NMR to fully characterise both the modified cyclodextrin based polymers and their chromium complexes. On a fundamental point of view it has been shown that chromate and dichromate do not interact with the same part of the material. Dichromates interact with the cavity whereas the chromates lie outside the cavity and interact preferentially with the carbonyl of the aliphatic bridging chain. Moreover, as it has been shown, it is possible to quantify the different constituents of these polymeric materials. The effects of the synthesis conditions can readily be visualised and the optimisation of the synthetic strategy is, therefore, possible. The main result concerning direct application of the present study is the discovery of a new class of stable materials that can be used for the extraction of chromium oxoanions from solutions. Very interestingly, we demonstrate that these materials are not degraded by the chromium oxanions although they are known for their strong oxidant properties that can easily degrade most of the polymers tested so far. Moreover, it is possible to regenerate the polymers by a simple chemical treatment such as reduction with sodium sulphite for instance. The starting polymer can be used for this purpose several times. The potential applications of these products on an industrial scale are presently under investigation.

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