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Polymer inclusion compounds of cyanoethylated β -cyclodextrin

RAPID COMMUNICATION

Summary — A cyanoethylated β -cyclodextrin (CE- β -CD) offered as a commercial product by the Industrial Chemistry Research Institute, Warsaw, has been characterized as heptakis-6-O-(2-cyanoethyl)- β -cyclodextrin of technical grade. Inclusion compounds with fluorobenzene, chloroform, chlorobenzene, tetrachloroethylene, vinylidene chloride, and dichlorodimethylsilane were obtained. Radiation polymerizations of vinylidene chloride and polycondensation of dichlorodimethylsilane were carried out in the adducts with CE- β -CD. Stable adducts of CE- β -CD with poly(vinylidene chloride) of 12.3 wt. % polymer content and with cyclic dimethylsiloxanes containing 4.66 mols of $-(\text{CH}_3)_2\text{SiO}-$ units per 1 mol of CE- β -CD were obtained.

Little is yet known about cyanoethylated cyclodextrins (CE-CDs). To our best knowledge the only source of information available in the literature concerning these CD derivatives is the patent granted to the Corn Products Company in 1969 [1]. According to the patent one can obtain CE-CDs of rather uncontrolled substitution. Nevertheless, cyanoethyl derivatives, easy to synthesize, can be important as host molecules as well as the starting substances to obtain new hosts, in which reactive cyano groups have been replaced. The cyano group can be transformed into almost any other of the known reactive functions.

EXPERIMENTAL

Cyanoethylated β -cyclodextrin

Cyanoethylated β -cyclodextrin (CE- β -CD) was a commercial product offered by ICRI. CE- β -CD was crystallized from methanol, chemical composition: C, 48.23%; H, 6.12%; N, 6.33%; IR spectrum (KBr): 2928–3395, 2926, 2248, 1680, 1368, 1156, 1079, 1032, 851, and 756 cm^{-1} . $^1\text{H-NMR}$ ($[\text{D}_6]$ DMSO): $\delta = 2.73$ ppm (t, 14H, $J = 5.82$, $-\text{CH}_2\text{CN}$); 4.88 ppm (d, 7H, $J = 2.67$, C1H); 5.75 and 5.82 ppm (14H, HO-2 and HO-3); 6.75, 6.89, 7.23 and 7.36 ppm (2H, CONH_2). $^{13}\text{C-NMR}$ ($[\text{D}_6]$ DMSO): $\delta = 18.17$ ppm ($-\text{CH}_2\text{CN}$); 35.49 ppm ($-\text{CH}_2\text{CO}$); 65.55 ppm ($-\text{CH}_2$); 70.53 ppm (C-5); 72.34 ppm (C-2); 73.05 ppm

(C-3); 82.02 ppm (C-4); 102.39 ppm (C-1); 119.48 ppm ($-\text{CN}$); 172.30 ppm (CO). FAB MS (M^+) m/z : 1506.7; 1528.6; 1546.6; 1599.8.

Preparation of CE- β -CD inclusion compounds with fluorobenzene, chlorobenzene, chloroform and tetrachloroethane. General procedure

CE- β -CD (1 g, $6.64 \cdot 10^{-4}$ mol) was dissolved in 300 mL of water and a guest substance was added to the solution with stirring. After 15 min, a precipitate was filtered off and dried over P_2O_5 , under a guest substance vapor pressure. In each case 0.5 g of guest substance was added to obtain: 0.98 g inclusion compound with fluorobenzene, 0.89 g with chlorobenzene, 0.3 g with chloroform, and 0.5 g with tetrachloroethane. CE- β -CD*fluorobenzene: $^1\text{H-NMR}$ ($[\text{D}_6]$ DMSO): $\delta = 4.87$ ppm (d, 7H, $J = 2.67$, C1H), 5.75 and 5.82 (14H, HO-2 + HO-3), 7.16–7.39 (m, 10H, Ar). CE- β -CD*chlorobenzene: chemical composition: C, 50.7%; H, 5.92%; N, 5.70%; Cl, 3.55%. CE- β -CD*chloroform: chemical composition: C, 42.44%; H, 5.59%; N, 5.17%; Cl, 6.22%. CE- β -CD*tetrachloroethane: chemical composition: C, 40.08%; H, 5.01%; N, 4.42%; Cl, 10.43%.

Preparation of CE- β -CD inclusion compounds with poly(vinylidene chloride) (PVDC)

CE- β -CD (2 g, $1.32 \cdot 10^{-3}$ mol) was dissolved in 600 mL of water and 1 g vinylidene chloride was added with stirring. After 30 min, a precipitate was filtered off and poured into glass ampoules. γ -Irradiation (5 Mr) was applied to initiate the polymerization reaction. The polymerization product (1.5 g) was dried over P_2O_5 . Che-

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mical composition: C, 42.62%; H, 5.97%; N, 4.32%; Cl, 9.04%. IR spectrum (KBr): 2928–3395 cm^{-1} ; 2226 cm^{-1} ; 1650 cm^{-1} ; 1430 cm^{-1} ; 1255 cm^{-1} ; 1156 cm^{-1} ; 1079 cm^{-1} ; 1032 cm^{-1} ; 851 cm^{-1} ; 756 cm^{-1} .

Preparation of CE- β -CD inclusion compounds with dichlorodimethylsilane (DCDMS)

CE- β -CD (1 g, $6.64 \cdot 10^{-4}$ mol) was dissolved in 300 mL of water and 4 g DCDMS was added with stirring. After 15 min, a precipitate was filtered off. The sediment was air-dried and then dried over P_2O_5 . The product was dissolved in 500 mL of water on heating. The precipitate obtained after cooling was filtered off and rinsed with water, acetone, ethyl acetate, acetone and water. The precipitate was dried over P_2O_5 (yield, 1.5 g). The IR spectrum shows additional bands at 1270, 910, 810 and 780 cm^{-1} when compared with that of CE- β -CD. $^1\text{H-NMR}$ ($[\text{D}_6]$ DMSO): $\delta = -0.0698, -0.0196, 0.0333, 0.0427$ and 0.1116 ppm (27H); 1.0168, 1.0403 and 1.0638 (2H); 2.73 (t, 14H, $J = 5.82$); 4.88 (d, 7H, $J = 2.67$); 5.75 and 5.82 (14H); 6.10 (s, 1H).

Apparatus

IR spectra were recorded on a Philips Analytical PU 9800 FTIR Spectrometer. $^1\text{H-NMR}$ spectra were recorded for solutions in $[\text{D}_6]$ DMSO on a Varian VXR 300 (300 MHz) Spectrometer. $^{13}\text{C-NMR}$ spectra were recorded at 75 MHz on a Varian VXR 300 Spectrometer with $[\text{D}_6]$ DMSO as a solvent. Mass spectra were obtained on a Finnigan Mat 95 with FAB ionization.

RESULTS AND DISCUSSION

A simple method of cyanoethylation of cyclodextrins with a limited control of substitution has now been developed at the Warsaw Technical University in cooperation with the Industrial Chemistry Research Institute (ICRI), Warsaw. The separation and purification process to get individual compounds is under way. Meanwhile, because chromatographic purifications are scale-limited, we have preliminarily examined the commercial product offered by ICRI in the hope that, in some cases, the product can be ready for use without further treatment.

It should be mentioned that only two CD derivatives are produced industrially [2]: methylated and hydroxypropylated β -CDs. Two companies, the Wacker Chemie (Germany) and one in Hungary, faced the same problem: what was required and what was economical if methylated and hydroxypropylated CDs were to be considered. Finally, they launched the production of randomly methylated β -CD, DS = 1.8, and 2-hydroxypropylated β -CD, DS = 2.8, ready for use [2].

The ICRI product was not an individual compound but is very close to heptakis-6-O-(2-cyanoethyl)- β -CD.

This finds a support in the results of the following investigations. Combustion analysis corresponds satisfactorily to the chemical composition of the product (N 6.33%, calcd. 6.51%). The IR absorption band at 2248 cm^{-1} can only be ascribed to cyano groups; $^1\text{H-NMR}$ spectroscopy shows the correct - $\text{CH}_2\text{CN}:\text{H-1}$ (anomeric) ratio equal just to 1:1 ($\delta = 2.73$ ppm, 14H and $\delta = 4.88$ ppm, 7H). The proton signal of HO-6 of glucose units ($\delta = 4.54$ ppm) disappears in the spectrum, while the signals of HO-2 and HO-3 of the units ($\delta = 5.75$ ppm and 5.82 ppm), collectively integrated (14H), show the ca. 2:1 correct ratio to the anomeric H1 signal.

$^{13}\text{C-NMR}$ indicates all the cyano groups to be entirely equivalent, represented by a single of the highest sharp signals ($\delta = 119$ ppm) in the spectrum. FAB mass spectroscopy shows pronounced peaks at m/z 1506.5 ($\text{M}+1$)⁺ and 1528.6 ($\text{M}+\text{Na}^+$), which correspond to the seven cyanoethyl groups in the β -CD molecule. However, in the mass spectrum other peaks are present at higher masses ($\text{M}+\text{Na}^+$): m/z 1546.6, 1599.8, which may correspond to β -CD molecules having six cyano plus one amide groups and seven cyano plus one amide groups, respectively. Amide groups appear as a result of partial hydrolysis which probably accompanies the cyanoethylation reaction. There is also a weak absorption band at 1680 cm^{-1} in the IR spectrum, which cannot exclude such groups in the ICRI product. Four small signals at $\delta = 6.75, 6.89, 7.23$ and 7.36 ppm, present in the $^1\text{H-NMR}$ spectrum as well as a minute signal at $\delta = 172$ ppm in the $^{13}\text{C-NMR}$ spectrum can also be assigned to the amide groups.

It can be concluded that the ICRI product is mainly heptakis-6-O-cyanoethylated β -CD having a small amount of amide groups as foreign functions.

In any case the product behaves like a receptor of the CD type and can be applied as such.

The product is soluble in water and hot methanol. From the water solution it produces inclusion compounds the same way as does the parent β -CD.

Adducts of CE- β -CD with fluorobenzene, chlorobenzene, chloroform and tetrachloroethane as guest molecules were obtained, 10.6; 11.2; 6.9; and 12.3 wt. % guest substance contents, respectively.

Not only a low molecular weight inclusion compound but also a polymer guest — cyanoethylated β -cyclodextrin system was easy to obtain. This was made possible by polymerization of vinylidene chloride included in the CE- β -CD. Polymerization by γ -irradiation initiation resulted in a stable polymer inclusion compound probably of the rotaxane structure like that obtained earlier in the parent β -cyclodextrin clathrate [6, 10]. The system contained 12.3% weight of the poly(vinylidene chloride) guest.

It was also interesting to examine interactions between CE- β -CD and dichlorodimethylsilane in order to compare results with those obtained previously for β -cyclodextrin [5].

In the presence of water several processes were possible:

1) Polycondensation of $(\text{CH}_3)_2\text{SiCl}_2$ to produce siloxane oligomers and polymers.

2) Clathration of $(\text{CH}_3)_2\text{SiCl}_2$ by CE- β -CD followed by hydrolysis and condensation (inside or outside the CE- β -CD lattice).

3) Silylation of OH groups in CE- β -CD.

There is ample evidence for the second process with inside condensation to have proceeded to produce inclusion compounds with cyclic dimethylsiloxanes, when parent β -CD is used [4]. The process was strongly confirmed additionally by using CE- β -CD, in which the most reactive primary hydroxyl groups have been blocked, making silylation less possible. The same procedure [5] gave a powder precipitate. IR spectrum of the powder contained absorption bands at 1270, 910, 810 and 780 cm^{-1} characteristic of dimethylsiloxanes [11], retaining the main part of the fingerprint of β -CD unchanged. $^1\text{H-NMR}$ clearly indicated that there was no silylation of CE- β -CD (correct ratio 2:1 of HO-2 + HO-3 to H-1). Additionally, there was no signal at $\delta = 57.8$ ppm in the $^{13}\text{C-NMR}$ spectra characteristic of the -Si-O-C- group [3]. The dimethylsiloxanes content was 4.66 moles of $-(\text{CH}_3)_2\text{SiO}-$ per 1 mol of CE- β -CD ($\text{CH}_3:\text{H-1} = 4$, with CH_3 at $\delta = 0.0698-0.1116$ ppm).

As a final conclusion it can be stated that the CE- β -CD offered by ICRI is essentially heptakis-6-O-(2-cyanoethyl)- β -CD of technical grade, ready for use in inclusion processes to produce low and macromolecular inclusion compounds.

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