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β-Cyclodextrins modified by alkyl and poly(ethylene oxide) chains: A novel class of mass transfer additives for aqueous organometallic catalysis

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ABSTRACT

A novel class of β-cyclodextrins (β-CDs) bearing alkyl chains on the secondary face and poly(ethylene oxide) chains on the primary face was synthesized. Their interactions with two water-soluble derivatives of triphenylphosphane were investigated by $^{31}P\{^{1}H\}$ and ^{1}H NMR. Their behaviour in rhodium-catalysed biphasic hydroformylation of 1-decene was evaluated and the best result was obtained with a β-CD bearing methyl groups on the secondary face and poly(ethylene oxide) chains on the primary face. This CD appeared to be more efficient than randomly methylated β-CD which is currently one of the best mass transfer additives for hydroformylation.

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1. Introduction

Heterogeneous and homogeneous catalytic processes are used to produce numerous value-added products. However, both approaches suffer from drawbacks. Homogeneous catalysts cannot be separated from the product and contaminate it whereas heterogeneous catalysts had a lower catalytic activity. In a green chemistry context, the replacement of organic solvents by water and the minimization of metal leaching are essential. This has led to the development of aqueous biphasic catalysis which can gather the positive aspects of both homogeneous and heterogeneous catalytic processes [1,2]. Unfortunately, numerous organic substrates display a weak solubility in water leading to a very low catalytic activity. In order to circumvent this major problem, the use of cyclodextrins (CDs) for aqueous biphasic organometallic catalysis was proposed in 1986 and is still the object of intensive research [3–10]. For instance, it was recently reported that CDs could be successfully used as mass transfer additive in alkylation [11,12], metathesis [13], telomerization [14] or polymerization [15] reactions. Some of us had deeply studied the role played by CDs in rhodium-catalysed biphasic hydroformylation of higher olefins [16]. The efficiency of CDs was attributed to the formation of an inclusion complex between the hydrophobic substrate and CD at the liquid/liquid interface which facilitates the reaction between the substrate and the water-soluble organometallic catalyst [17–19]. In addition, it was demonstrated that one of the essential points is to synthesize a surface-active CD which does not interact with the water-soluble phosphanes. From NMR and catalytic studies, it was proposed that a not-interacting β-CD has to be encumbered on the secondary face by alkyl groups and has to possess hydrophilic groups on the primary face. For instance, some β-CDs bearing alkyl chains on the secondary face and sulfoalkyl chains on the primary face were synthesized and had proved to be a really efficient mass transfer additive [20,21].

In our continuing research of better modified CDs, we report hereby a novel class of β-CDs bearing alkyl groups on the secondary face and poly(ethylene oxide) (PEO) chains on the primary face (Scheme 1). Methyl or heptyl groups were covalently linked on the secondary face of β-CD to evaluate the effect of chain length on the complexing properties. On the primary face, PEO chains

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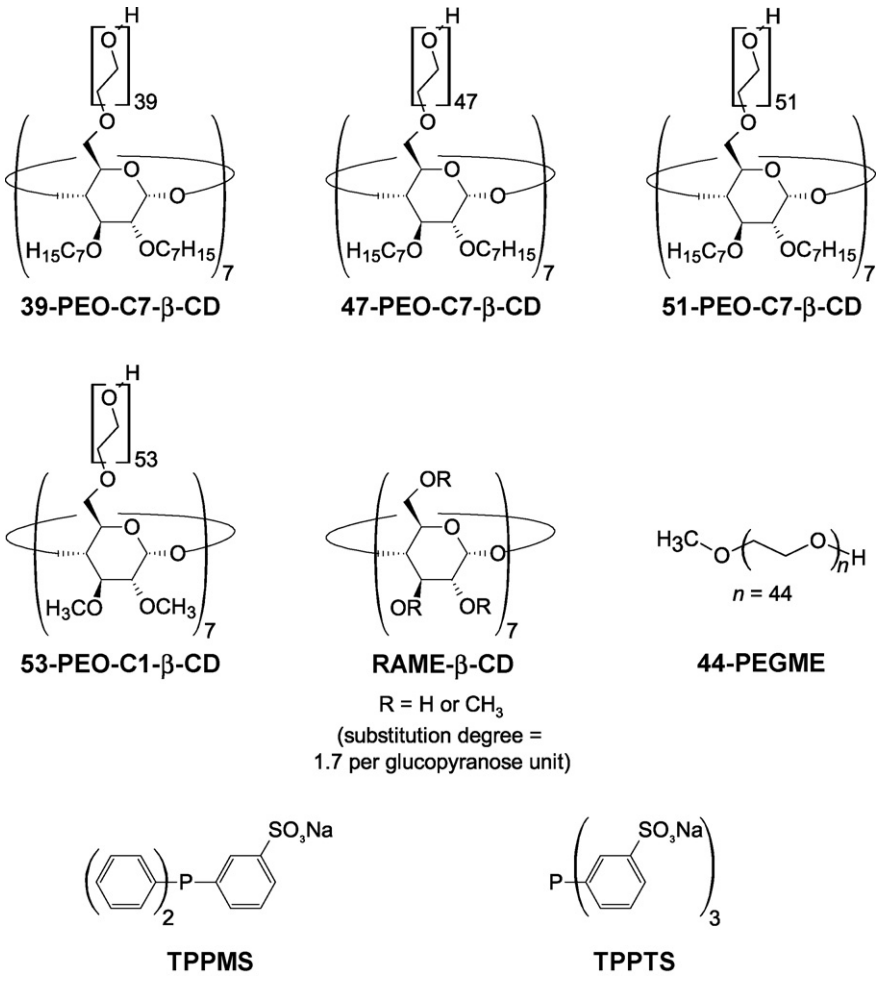


Scheme 1. Structures of β-cyclodextrin derivatives, linear oligo(ethylene oxide) derivative and water-soluble ligands used in this work. The poly(ethylene oxide)-alkyl-β-CDs have been named by acronyms of the type *n*-PEO-C*n*′-β-CD where *n* is the average number of ethylene oxide units per branch and C*n*′ is the length of the alkylchain.

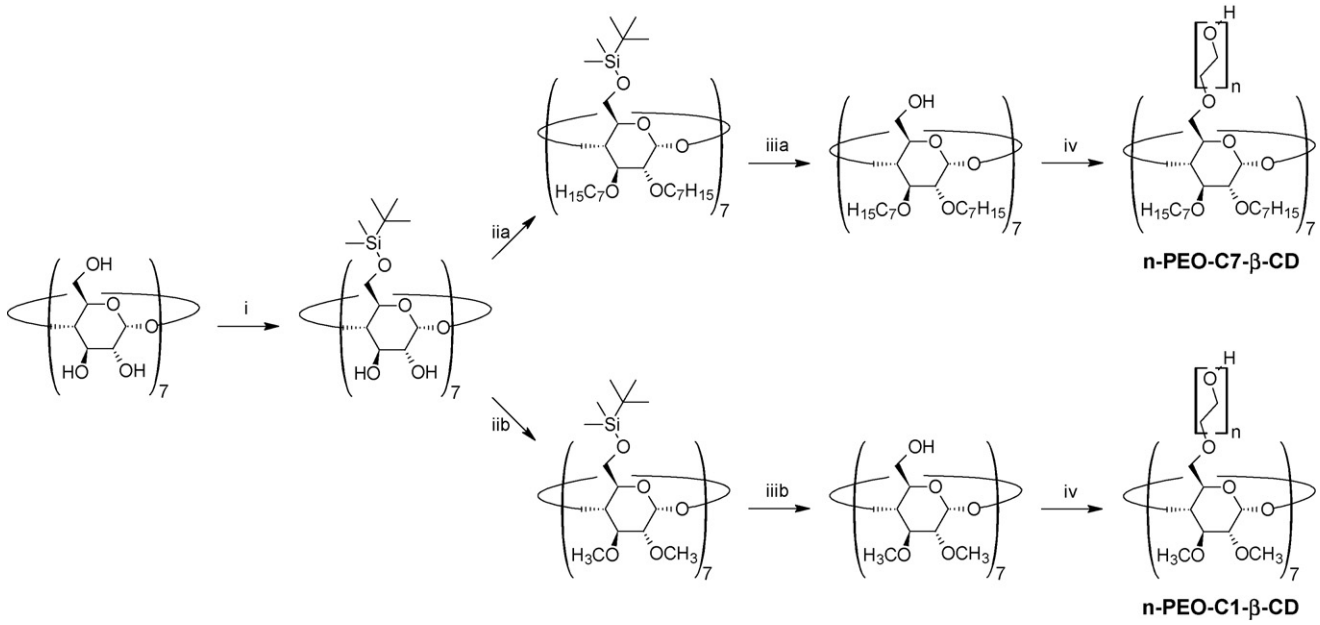
were grafted to confer a high hydrophilic character. The polymerization degree was chosen in order to obtain a cloud point higher than the temperature of the reaction (80 °C). The way these PEO-alkyl-β-CDs interacted with two water-soluble derivatives of triphenylphosphane (Scheme 1) and the behaviour of these CDs in rhodium-catalysed biphasic hydroformylation were investigated.

2. Experimental

2.1. Materials and apparatus

All chemicals were purchased from Acros Organics and Sigma–Aldrich in their highest purity. Dicarbonylacetylacetonato rhodium(I), polyethylene glycol methyl ether (MW = 2000 g mol^{-1}) and deuterated solvents were purchased, respectively, from Strem Chemicals, Sigma–Aldrich and Euriso-Top in their highest purity and used without further purification. β-CD and RAME-β-CD were purchased from Roquette Frères and Wacker Chemie GmbH, respectively. β-CD was dried under vacuum at 80 °C during 16 h before using. RAME-β-CD was of pharmaceutical grade (Cavasol® W7M Pharma) and its degree of substitution was equal to 1.7 [22]. RAME-β-CD was used as received. The sodium salt of tris(3-sulfonatophenyl)phosphane (TPPTS—P(*m*-$C_6H_4SO_3Na)_3$) was synthesized as reported by Gärtner et al. [23]. The sodium salt of diphenyl(3-sulfonatophenyl)phosphane (TPPMS—$(C_6H_5)_2P$(*m*-$C_6H_4SO_3Na$)) was prepared by a literature method [24]. The purity of the two water-soluble phosphanes was carefully controlled. In particular, ^1H and $^{31}P\{^1H\}$ NMR analysis indicated that the water-soluble phosphanes were only sulfonated in *meta* position and less than 1% of its oxide was present. Carbon monoxide/hydrogen mixture (1:1) was used directly from cylinders (>99.9% pure; Air Liquide). Distilled deionized water was used in all experiments. All solvents and liquid reagents were degassed by bubbling nitrogen for 15 min or by two freeze–pump–thaw cycles before use. All the high-pressure hydroformylation experiments were carried out in a 25 mL stainless steel autoclave supplied by Parr. Gas chromatographic analyses were carried out on a Shimadzu GC-17A gas chromatograph equipped with a methyl silicone capillary column (30 m × 0.32 mm) and a flame ionization detector (GC:FID). The ^1H and $^{31}P\{^1H\}$ NMR spectra performed to investigate the interactions between CDs and phosphanes were recorded at 300.13 and 121.49 MHz, respectively, on a Bruker Avance DRX300 instrument. Chemical shifts in ^1H and $^{31}P\{^1H\}$ NMR are given in parts per million (ppm) relative to external references sodium [D_4]3-(trimethylsilyl)propionate (98% atom D) in D_2O for ^1H NMR and H_3PO_4 in H_2O for $^{31}P\{^1H\}$ NMR.

The ^1H and ^{13}C (data not showed) NMR performed to characterize the CD derivatives were recorded on a Bruker spectrometer (^1H, 300.13 MHz and ^{13}C, 75.5 MHz) using DMSO-d_6 or chloroform ($CDCl_3$) as solvents at 20 °C. The molar masses were determined by size exclusion chromatography (SEC) with THF as eluent. SEC was calibrated using linear poly(ethylene oxide) samples. The molecu-



Scheme 2. Synthetic strategy for PEO-alkyl-β-CDs from β-cyclodextrin: (i) *tert*-butylchlorodimethylsilane, pyridine; (iia) 1-bromoheptane, sodium hydride, THF/DMF (50/50); (iib) iodomethane, sodium hydride, THF; (iiia) tetrabutylammonium fluoride, THF; (iiib) ammonium fluoride, methanol and (iv) ethylene oxide, DPMK, THF.

lar weights of the star polymers are then calculated considering the functionality of the initiator [25].

2.2. Synthesis of β-CD derivatives

The first step of the chemical modification was the synthesis of heptakis(6-*O*-tert-butyldimethylsilyl)-β-CD. This protection of the β-CD primary face with tert-butyldimethylsilane was common to both alkyl CD derivatives and was described by Fügedi [26]. Heptakis(2,3-di-*O*-heptyl)-β-CD was synthesized according to the procedure described by some of us [27]. Heptakis(6-*O*-tert-butyldimethylsilyl-2,3-di-*O*-heptyl)-β-CD was deprotected by using tetrabutylammonium fluoride (TBAF) [28]. Heptakis(2,3-di-*O*-methyl)-β-CD was synthesized according to the procedure described by Takeo et al. [29,30]. The deprotection of the primary hydroxyl functions of heptakis(6-*O*-tert-butyldimethylsilyl-2,3-di-*O*-methyl)-β-CD was successfully achieved by using ammonium fluoride [31].

The polymerization conditions were previously described by some of us in the case of the heptyl derivatives and the same conditions were nearly used for the methyl derivatives [32].

The synthesis of heptakis(6-*O*-PEO-2,3-di-*O*-methyl)-β-CD from heptakis(2,3-di-*O*-methyl)-β-CD is described here to illustrate a typical synthesis. The polymerization reactions were carried out at 40 °C under high vacuum in a 250 mL four-neck flask equipped with a magnetic stirrer, an inlet, and three burets containing ethylene oxide, diphenylmethylpotassium (DPMK) and the anhydrous precursor CD derivative dissolved in THF (the final hydroxyl concentration was $[OH^-] = 3 \times 10^{-2}$ mol L^{-1}). CD was first introduced and it was followed by the slow addition of DPMK. The orange-red color of the deprotonating agent becomes yellow when the alkoxides were formed. The obtained homogenous solution was stirred during 48 h at room temperature. It was cooled to 0 °C before adding ethylene oxide ([OE] = 3 mol L^{-1}) and then warmed at 40 °C for 9 days. The alkoxides were deactivated by adding a small quantity of HCl (10%) in methanol (3 mL). The solution was concentrated and then precipitated twice in cold diethyl ether and once in cold pentane. The heptakis(6-*O*-PEO-2,3-di-*O*-methyl)-β-CD was obtained with a yield of 45%.

2.3. General procedure for the hydroformylation reaction

All catalytic reactions were performed under nitrogen using standard Schlenk techniques. All solvents and liquid reagents were degassed by bubbling nitrogen for 15 min or by two freeze–pump–thaw cycles before use. $Rh(acac)(CO)_2$ (4.07×10^{-3} mmol), TPPTS (0.021 mmol), chemically modified CD (0.0068 mmol) or polyethylene glycol methyl ether (0.0472 mmol) were dissolved in 1.2 mL of water. The resulting aqueous phase and an organic phase composed of olefin (5.50 mmol) and undecane (0.203 mol—GC internal standard) were charged under an atmosphere of nitrogen into the 25 mL reactor, which was heated at 80 °C. Mechanical stirring equipped with a multipaddle unit was then started (1500 rpm) and the autoclave was pressurized with 50 atm of CO/H_2 (1/1) from a gas reservoir connected to the reactor through a high-pressure regulator valve allowing to keep constant the pressure in the reactor throughout the whole reaction. The reaction medium was sampled after 24 h of reaction for GC analyses of the organic phase after decantation. For kinetic measurements the time corresponding to the addition of CO/H_2 was considered as the beginning of the reaction.

2.4. Recycling experiments

The initial run was carried out as described above. After reaction, the autoclave was cooled to room temperature and CO/H_2 pressure was carefully evacuated. The biphasic system was transferred out of the autoclave under a nitrogen atmosphere. After decantation, the

Table 1
Characteristics of PEO-β-CD conjugates.

Cyclodextrin	Mn_{SEC} (g mol^{-1})[a]	Mn_{NMR} (g mol^{-1})[b]	PDI[c]
39-PEO-C7-β-CD	11 700	14 600	1.05
47-PEO-C7-β-CD	13 500	17 000	1.05
51-PEO-C7-β-CD	14 500	18 300	1.10
53-PEO-C1-β-CD	17 700	17 900	1.06

[a] Calculated from SEC chromatograms taking into account the seven arms of the PEO.
[b] Determined by ^{1}H NMR.
[c] Determined by SEC chromatography.

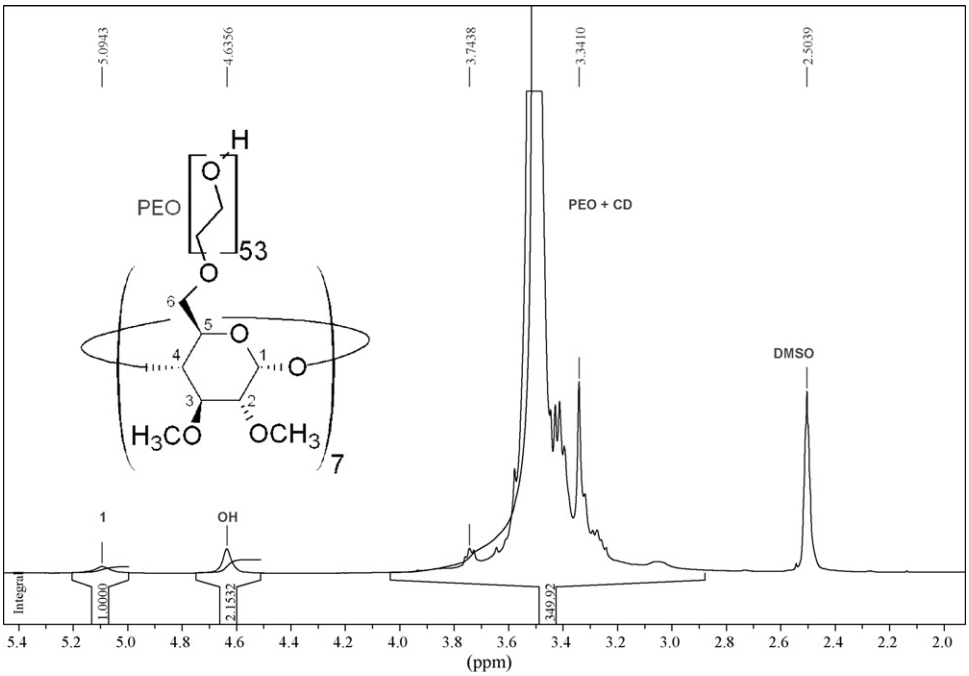


Fig. 1. ^{1}H NMR spectrum of 53-PEO-C1-β-CD in DMSO-d_6 at 25 °C.

bulk organic solution was removed. The catalytic aqueous layer and a new organic phase (composed of 1-decene (5.50 mmol) and undecane (0.203 mmol)) were introduced in the autoclave. Then, the first recycling was carried out using the same procedure as described above. The overall recycling procedure was then repeated for the second recycling.

3. Results and discussion

3.1. Synthesis

The synthesis of poly(ethylene oxide)-alkyl-β-cyclodextrins (PEO-alkyl-β-CDs) was achieved in a multi-steps procedure. First, the synthesis of CD initiators was conducted by using already reported procedures and then, the polymerization of ethylene oxide was carried out thanks to an anionic ring opening polymerization (Scheme 2).

The synthesis of heptakis(6-*O*-tert-butyldimethylsilyl)-β-CD was first carried out to obtain a selective modification of the primary face of β-CD [26]. Then, heptakis(6-*O*-tert-butyldimethylsilyl)-β-CD was reacted with bromoheptane or iodomethane to generate heptakis(6-*O*-tert-butyldimethylsilyl-2,3-di-*O*-alkyl)-β-CDs. The deprotection of the primary face was conducted with ammonium fluoride for the methyl derivative [31] and with tetrabutylammonium fluoride for the heptyl derivative [28]. This procedure allowed generating the primary hydroxyl functions which had the same reactivity toward the subsequent ethylene oxide polymerization. The ethylene oxide polymerization with heptakis(2,3-di-*O*-heptyl)-β-CD was already reported and depended on the polymerization time. The number of ethylene oxide units per PEO branches might vary from 39 to 51 (Table 1) [32]. The synthesis of heptakis(6-*O*-PEO-2,3-di-*O*-methyl)-β-CD was carried out under vacuum in THF. A key step of this polymerization was to remove all the water molecules entrapped in the CD derivative. The best results were obtained by distillation of heptane followed by distillation of benzene. This polymerization was undertaken by addition of a THF solution of heptakis(2,3-di-*O*-methyl)-β-CD. Then, a diphenylmethylpotassium (DPMK) solution was added. The molar ratio hydroxyl/DPMK was set to 5 in order to prevent the initiator precipitation. All the primary hydroxyl groups could take part to the polymerization step thanks to the fast kinetic exchange between hydroxyl and hydroxylate forms [33]. Forty-eight hours after this metallation

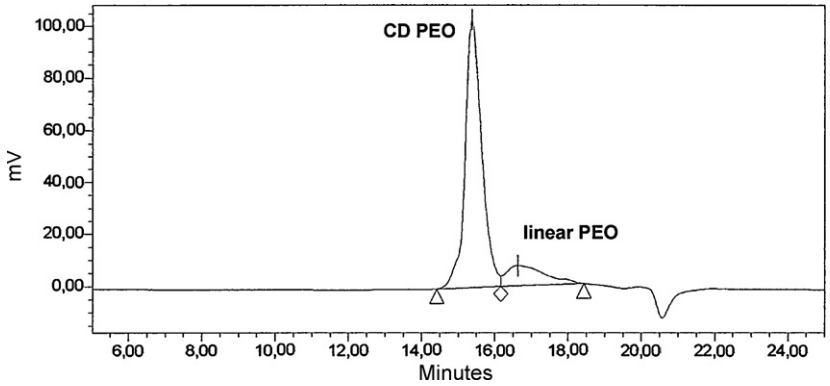


Fig. 2. Size exclusion chromatogram of 53-PEO-C1-β-CD carried out in THF at RT.

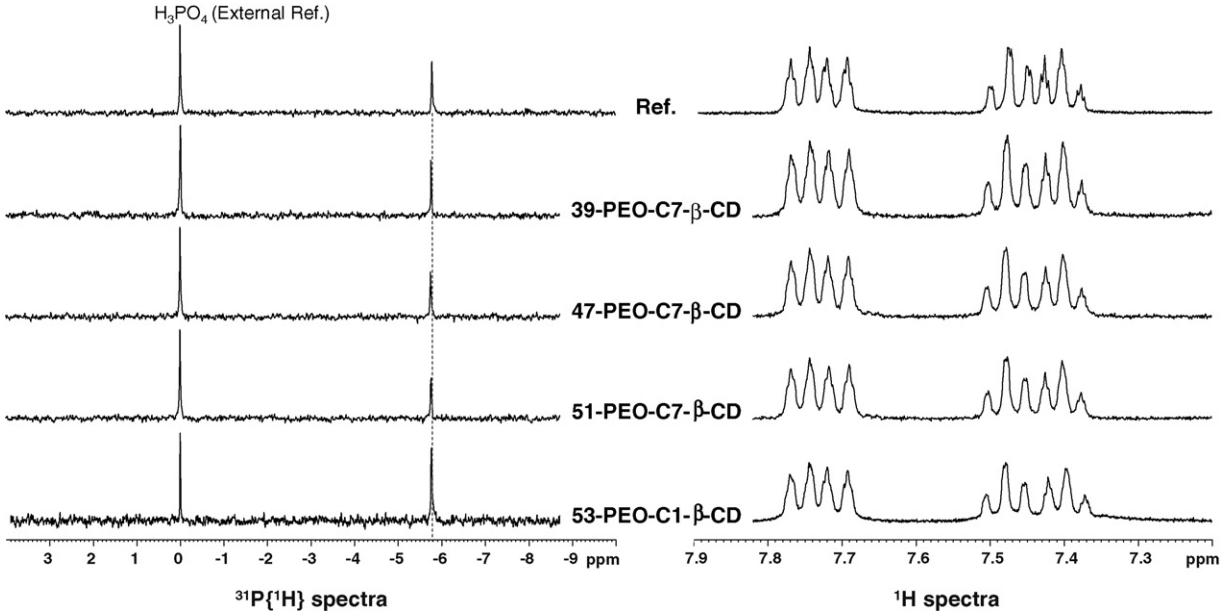


Fig. 3. Partial $^{31}P\{^{1}H\}$ and ^{1}H NMR (aromatic part) spectra of TPPTS (1 mM) in D_2O at 25 °C in the presence of various PEO-alkyl-β-CDs (1 mM).

step, ethylene oxide was introduced in the reactor. The characteristics of this polymerization and those obtained for the various heptakis(6-*O*-PEO-2,3-di-*O*-heptyl)-β-CDs are reported in Table 1.

The polymerization yield was low and witnessed a very slow polymerization kinetic. The NMR (Fig. 1) and SEC (Fig. 2) analyses provide similar molecular weights (taking into account the star correction for the SEC) [25] and the polydispersity index (PDI) was pretty low (Table 1).

This result was in accordance with the living ethylene oxide polymerization initiated by heptakis(2,3-di-*O*-heptyl)-β-CD. A careful analysis of the size exclusion chromatogram showed a large peak corresponding to the expected molecule, and a small peak in the low molecular weight region (Fig. 2). This last population had a molecular weight close to 2000 g mol^{-1}, and corresponded to α,ω-dihydroxy-PEO. The molecular weight of this side population was close to the one of each branch of the poly(ethylene oxide)-alkyl-β-CDs, indicating that water molecules might still be entrapped in the CD derivatives and participated to the polymerization. It was already reported that such ethylene oxide polymerizations initiated with CD-based initiators occurred in living conditions [32]. We assumed that it took place in the same way as our conditions as suggested by the low polydispersity indexes of the polymers.

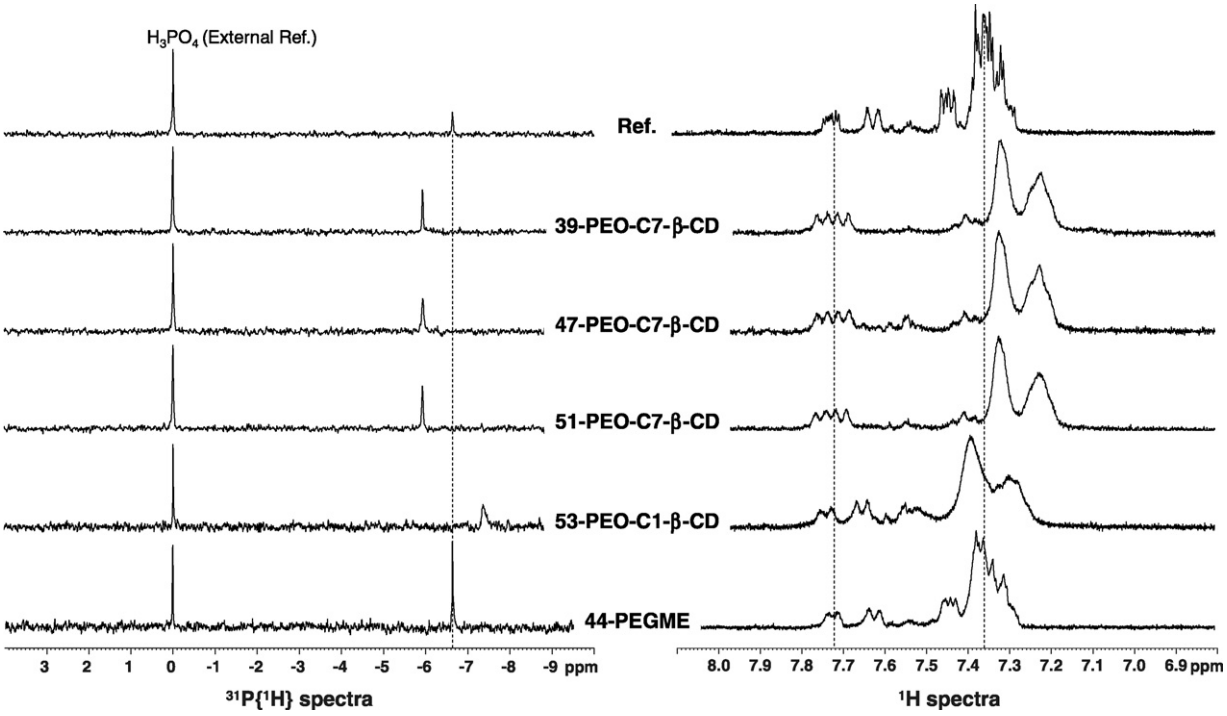
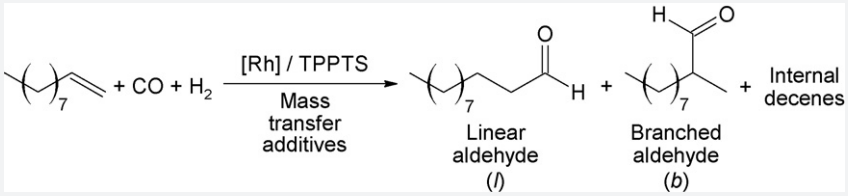


Fig. 4. Partial $^{31}P\{^{1}H\}$ and ^{1}H NMR (aromatic part) spectra of TPPMS (1 mM) in D_2O at 25 °C in the presence of various PEO-alkyl-β-CDs (1 mM) or linear oligo(ethylene oxide) derivative (7 mM).

Table 2
Biphasic rhodium-catalysed hydroformylation of 1-decene with TPPTS as water-soluble ligand in the presence of different additives[a].



Entry	Additives	Conversion (%)[b]	Selectivity (%)[c]	*l*/*b* ratio[d]	Phase separation[e]
1	–	1	61	2.8	+
2	RAME-β-CD	29	95	1.8	+
3	39-PEO-C7-β-CD	31	95	2.8	–
4	47-PEO-C7-β-CD	30	98	2.8	–
5	51-PEO-C7-β-CD	26	98	2.8	–
6	53-PEO-C1-β-CD	61	89	2.5	+
7	44-PEGME	33	89	2.7	–
8	53-PEO-C1-β-CD[f]	56	90	2.5	+
9	53-PEO-C1-β-CD[g]	58	89	2.6	+

[a] *Experimental conditions*: $Rh(acac)(CO)_2$ (4.07×10^{-3} mmol), TPPTS (0.021 mmol), cyclodextrin (0.0068 mmol) or polyethylene glycol methyl ether (0.0472 mmol), H_2O (1.2 mL), 1-decene (5.50 mmol), undecane (0.203 mmol) 1500 rpm, *T*: 80 °C, *P*(CO/H_2: 1/1) = 50 bar, time: 24 h.
[b] Olefin conversion after 24 h (calculated with respect to the starting olefin).
[c] Aldehydes selectivity after 24 h, *i.e.* (mol. of aldehydes)/(mol. of converted olefins) × 100. The side products were mainly isomeric olefins.
[d] Ratio of linear to branched aldehyde product after 24 h.
[e] The separation between the aqueous and organic phases is reported according to the following convention: –, formation of an emulsion; +, good and fast phase separation.
[f] First recycling.
[g] Second recycling.

3.2. Interaction of PEO-alkyl-β-CDs with water-soluble triphenylphosphanes

The behaviour of PEO-alkyl-β-CDs with water-soluble phosphanes such as the sodium salt of meta-substituted trisulfonated triphenylphosphane (TPPTS) and the sodium salt of meta-substituted monosulfonated triphenylphosphane (TPPMS) (Scheme 1) was investigated by NMR spectroscopy. The $^{31}P\{^1H\}$ and ^1H NMR spectra of 1:1 mixture of PEO-alkyl-β-CDs and TPPTS were very similar to those obtained for free TPPTS (Ref.), indicating that no interaction between both constituents took place (see Fig. 3).

The absence of interaction between these PEO-alkyl-β-CDs and TPPTS was attributed to the presence of alkyl groups on the CD secondary face rather than the presence of PEO groups on the CD primary face. Indeed, some of us shown that the steric hindrance generated by the presence of methyl groups on the secondary face was sufficient to impede TPPTS penetration into the β-CD cavity [21]. In the case of TPPMS, the ^1H and $^{31}P\{^1H\}$ NMR spectra of 1:1 mixture of PEO-alkyl-β-CDs and TPPMS were different to those obtained for free TPPMS (Ref.—Fig. 4). In order to ensure that these modifications in NMR spectra were really due to CD skeleton and not to the PEO chains, the same NMR experiments were performed in the presence of a polyethylene glycol methyl ether (44-PEGME—the polymerization degree is equal to 44 and close to that of PEO-alkyl-β-CDs). Contrary to PEO-alkyl-β-CDs, no change was observed for TPPMS spectra in the presence of 44-PEGME.

Chemical shift changes on ^1H NMR spectra were observed for the aromatic protons of TPPMS in the PEO-alkyl-β-CD/TPPMS mixtures compared to pure TPPMS. For each PEO-C7-β-CD mixed with TPPMS, the three obtained spectra were similar. It was not the case for PEO-C1-β-CD for which the spectrum was different from the three others. These different results suggested that the interactions between TPPMS and these PEO-alkyl-β-CDs depended on the CD nature. In order to illustrate these different behaviours, 2D T-ROESY experiments were performed to observe ^1H–^1H homonuclear dipolar interactions between TPPMS and PEO-alkyl-β-CDs. Unfortunately, the interpretation of these spectra was impossible because of a spectral overlap between the internal protons of CD and the protons of PEO chains. The modifications observed on the $^{31}P\{^1H\}$ NMR spectra for TPPMS in the presence of PEO-alkyl-β-CDs were particularly informative. Indeed, the $^{31}P\{^1H\}$ signals appeared to be upfield or downfield shifts according to the alkyl group linked on PEO-alkyl-β-CDs. Actually, the $^{31}P\{^1H\}$ signal of TPPMS was downfield shifted in the presence of the three PEO-C7-β-CDs whereas an upfield shift was observed in the presence of PEO-C1-β-CD. These results suggested that a part of TPPMS was included into the PEO-C1-β-CD cavity whereas TPPMS formed external adduct with the heptyl chains of PEO-C7-β-CDs. Indeed, some of us had previously demonstrated that an upfield shift in $^{31}P\{^1H\}$ signal was synonymous with a formation of genuine inclusion complexes whereas a downfield shift corresponded to a modification of the phosphane environment [21,34,35]. For PEO-C7-β-CDs, the accessibility of the cavities was strongly reduced for TPPMS because of sterically demanding heptyl chains on the secondary face. The presence of these chains probably prevented from the formation of genuine inclusion complexes. In fact, it was already described in the case of amphiphilic CDs that the access to the cavity depended on the grafted chain length and the substituted face [36,37].

3.3. Catalysis

The effect of these different PEO-alkyl-β-CDs on the activity, the chemoselectivity and the regioselectivity was evaluated in the rhodium-catalysed hydroformylation reaction of 1-decene in an organic–aqueous biphasic system using $Rh(acac)(CO)_2$ as catalyst precursor and TPPTS as water-soluble ligand. TPPTS was preferred to TPPMS since this latter did not interact with the PEO-alkyl-β-CDs. As a comparison, the results without CD and with commercial randomly methylated β-CD (RAME-β-CD) are also presented in Table 2. The presence of any chemically modified β-CDs had a beneficial effect on the activity and the selectivity (Table 2).

Surprisingly, similar conversions were reached in the presence of any PEO-C7-β-CDs whatever the number of ethylene oxide units was. Unfortunately, a formation of an emulsion at the end of reaction was observed and the separation between the aqueous and organic layers was impossible. A reduction of the alkyl chain length

on the secondary face of PEO-alkyl-β-CD had a beneficial effect on the conversion. Indeed, the conversion was twice higher in the presence of PEO-C1-β-CD compared to PEO-C7-β-CDs. In addition, in the case of PEO-C1-β-CD, no emulsion was observed at the end of the reaction and the separation between the organic and the aqueous layer was very fast. To ensure that this positive effect on the conversion was well due to the CD skeleton, the same experiment was performed by replacing PEO-C1-β-CD by 44-PEGME. In the presence of 44-PEGME, the conversion was lower (33% compared to 61%) and at the end of the reaction, the separation between the aqueous and organic layers was not easy. So, the positive effect of PEO-C1-β-CD was unambiguously attributed to its complexing properties. Interestingly, PEO-C1-β-CD appeared more efficient in terms of activity than RAME-β-CD which is one of the best mass transfer additives in rhodium-catalysed biphasic hydroformylation of higher olefins [16].

The effect of these CDs on the chemoselectivity (the selectivity in aldehydes versus isomerisation products) was also studied. No marked difference among the various PEO-alkyl-β-CDs was observed since the values increased from 60% (without CD) to at least 89% in the presence of any CDs.

Concerning the regioselectivity, the linear to branched aldehydes ratio (*l*/*b*) varied from 2.8 (without CD) to 1.8 (in the presence of RAME-β-CD). As already described, this decrease was attributed to the formation of 1:1 inclusion complexes between TPPTS and RAME-β-CD [38,39]. Actually, these inclusion complexes induced the formation of phosphane low-coordinated rhodium species responsible for the decrease in linear to branched aldehydes ratio [40]. In the presence of PEO-alkyl-β-CDs, the value of the *l*/*b* ratio varied from 2.5 to 2.8 for PEO-C1-β-CD and PEO-C7-β-CDs, respectively. So, all these PEO-alkyl-β-CDs gave similar proportions of linear and branched aldehydes. Indeed, when the *l*/*b* ratio varied from 2.5 to 2.8, the percentages were equal to 71.4% and 73.7% for linear aldehydes and 28.6% and 26.3% for branched aldehydes, respectively. These data confirmed that no modification of the catalytic species occurred during the reaction when these PEO-alkyl-β-CDs were used as mass transfer additives.

Finally, it is important to underline that the catalytic system was totally recyclable in the presence of the best mass transfer additive (PEO-C1-β-CD). Indeed, conversion, chemoselectivity and regioselectivity were nearly unchanged after two recycling experiments (see Table 2; entries 6 and 8–9).

4. Conclusion

In our continuing research of an ideal mass transfer additive based on CDs, a β-CD bearing methyl chains on the secondary face and PEO chains on the primary face appears to be an attractive candidate for rhodium-catalysed biphasic hydroformylation of 1-decene since high activity and selectivity were reached. Indeed, the cavity of this CD is sufficiently accessible for the substrate while it is too narrow to interact with the water-soluble phosphane (TPPTS). Interestingly, this CD appeared more efficient in terms of activity and regioselectivity than randomly methylated β-CD which is one of the best mass transfer additives for hydroformylation. In addition, the chemoselectivity obtained in the presence of both CD was similar. Finally, the catalytic system was totally recyclable in the presence of this CD. We are currently working to synthesize new PEO-methyl-β-CDs with shorter PEO chains.

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