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Inclusion Complexes of Perfluorinated Oligomers with Cyclodextrins

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Received February 28, 2003

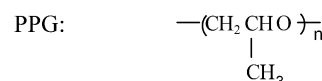
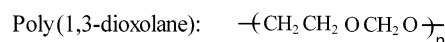
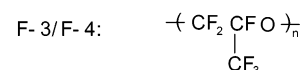
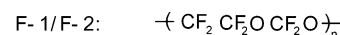
Revised Manuscript Received April 16, 2003

Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides of six to eight glucose units linked by α -1,4 linkages, which are called α -, β -, and γ -CD, respectively. They have a hollow truncated cone shape with various cavity sizes and microheterogeneous environment, which gives CDs the ability to form inclusion complexes (ICs) with various low molecular weight compounds^{1–3} and oligomers/polymers^{4–31} through noncovalent interactions. It has been well established that linear oligomers/polymers with either hydrophilic or hydrophobic nature can thread through CD channels and form stoichiometric inclusion complexes with a columnar structure.^{4–21} The driving force for the IC formation is intermolecular hydrogen bonding between neighboring CDs as well as steric compatibility and hydrophobic interactions between CD and oligomer/polymer.^{7,10,18} A good correlation between the cross-sectional areas of the oligomers/polymers and the cavity size of the CDs has been established.⁹ For example, poly(ethylene glycol) (PEG) forms inclusion complexes with α -CD^{4,6} and γ -CD⁷ while poly(propylene glycol) (PPG) forms inclusion complexes with β -CD and γ -CD.^{5,8} On the other hand, poly(1,3-dioxolane) forms ICs with α -, β -, and γ -CD.²⁵ It is believed that the study of inclusion complexes provides an approach to investigate the behavior of single polymer chain or two side-by-side parallel chains in isolated and well-defined environments.^{13,14}

To our knowledge, there has been no study on the inclusion complexes between fluorinated oligomers and CDs. Compared to their fully hydrogenated analogues, perfluorinated oligomers behave very differently in their interactions with both organic compounds and water.³² Moreover, the larger radius of fluorine compared to hydrogen leads to larger cross-sectional areas and different conformations of the fluorinated oligomers. Thus, it is of interest to investigate the complexation behavior between fluorinated oligomers and CDs. Here we report our study on the inclusion complexes of perfluorinated oligomers (F-oligomers) with CDs. It will be shown that oligo(tetrafluoroethylene oxide-*co*-difluoromethylene oxide) forms ICs with β - and γ -CD whereas its hydrogenated analogue poly(1,3-dioxolane) forms ICs with α -, β -, and γ -CD.²⁵ On the other hand, oligo(hexafluoropropylene oxide) forms IC with γ -CD

Scheme 1. Chemical Structures of Oligomers/Polymers



whereas its hydrogenated analogue PPG forms ICs with β - and γ -CD.^{5,8}

Experimental Section

Materials. Oligo(tetrafluoroethylene oxide-*co*-difluoromethylene oxide) α,ω -diol (ethylene:methylene = 1:1; number-average molecular weight (M_n) = 2000) (F-1), oligo(tetrafluoroethylene oxide-*co*-difluoromethylene oxide) α,ω -diol (ethylene:methylene = 1:1; M_n = 3800) (F-2), oligo(hexafluoropropylene oxide) (M_n = 2400) (F-3), oligo(hexafluoropropylene oxide) (M_n = 4600) (F-4), and PPG (M_n = 2000) were all supplied by Aldrich. The structures of the oligomers/polymers are shown in Scheme 1. α -CD and γ -CD were obtained from Tokyo Kasei, Japan; β -CD was supplied by Acros Organics. All CDs were dried at 80 °C in vacuo for at least 12 h before use.

Preparation of Inclusion Complexes. The oligomer was mixed with a saturated aqueous solution of CD at room temperature, and the mixture was stirred at room temperature for 2 days. The product that precipitated was collected by centrifugation, washed with water, and dried in vacuo at 60 °C. β -CD/PPG and γ -CD/PPG inclusion complexes were prepared following the procedures reported in the literature.^{5,8}

Stoichiometry Determination (Continuous Variation Method). The mole fraction of CD was varied from 0 to 1.0. In all cases, the sum of the amounts of CD and monomer unit of polymer was fixed at 3.5×10^{-4} mol, wherein the monomer unit of F-1 or F-2 is regarded as that shown in Scheme 1 on the basis that the mole ratio of methylene to ethylene is 1:1. The complexes that precipitated were separated by centrifugation, washed with water, and dried.

Measurements. XRD patterns of the complexes were recorded on a Siemens D5005 X-ray powder diffractometer with Cu K α (1.54051 Å) radiation (40 kV, 40 mA). Powder samples were mounted on a sample holder and scanned with a step size of $2\theta = 0.01^\circ$ between $2\theta = 3^\circ$ and 50° .

FTIR spectra were recorded on a Bio-Rad 165 FTIR spectrophotometer; 32 scans were signal-averaged at a resolution of 2 cm⁻¹. For measurements at elevated temperatures, a SPECAC high-temperature cell, equipped with an automatic temperature controller, was used. The complex was ground with KBr and compressed to form a disk.

¹³C CP/MAS NMR spectra were measured on a Bruker DRX-400 NMR spectrometer with a sample spinning rate of 8.0 kHz at room temperature. The spectra were acquired with a 2.75 μ s proton 90° pulse, a 3 ms contact time, and a 3 s repetition time.

Results and Discussion

The stoichiometry of the complexes was studied by the continuous variation method.^{11,20} Figure 1 shows the continuous variation plots for the formation of β -CD/F-1 and γ -CD/F-2 ICs. The sum of the amounts of CD

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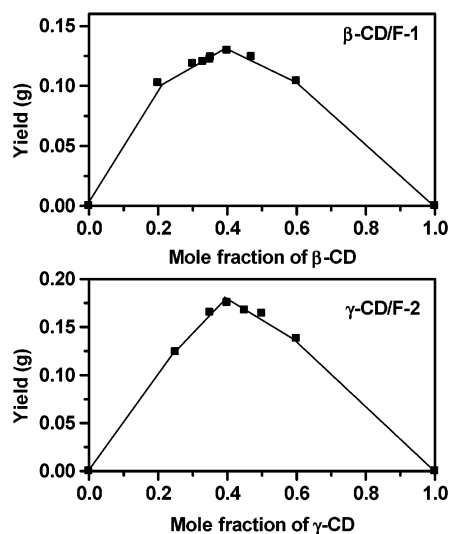


Figure 1. Continuous variation plots for complex formation between β -CD and F-1 and that between γ -CD and F-2.

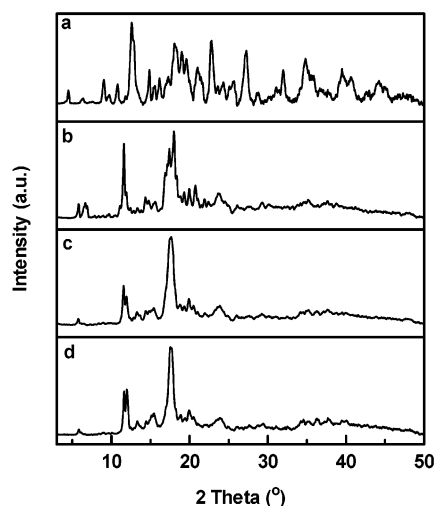


Figure 2. X-ray diffraction patterns for β -CD (a), β -CD/PPG IC (b), β -CD/F-1 IC (c), and β -CD/F-2 IC (d).

and monomer unit of polymer was all fixed at 3.5×10^{-4} mol. Maximum yields of ICs were obtained when the mole fraction of CD in the feed was about 0.40. Similarly, maximum yields of γ -CD/F-1, β -CD/F-2, γ -CD/F-3, and γ -CD/F-4 ICs were obtained when the mole fractions of CD in the feed were 0.43, 0.35, 0.32, and 0.30, respectively. The depth of a CD molecule is roughly 1.3 times the fully stretched length of the repeat unit of F-1/F-2. If CD forms a 1:1 complex with F-1/F-2, the complex would contain 0.43 mole fraction of CD. On the other hand, the depth of a CD molecule is 2.1 times the fully stretched length of the repeat unit of F-3/F-4. A 1:1 CD complex with F-3/F-4 would then contain 0.32 mole fraction of CD. Thus, the continuous variation method shows that, with the exception of β -CD/F-2 IC, the stoichiometry of the other ICs is close to 1:1.

Figure 2 shows the XRD patterns of β -CD, β -CD/PPG IC, β -CD/F-1 IC, and β -CD/F-2 IC. Although the relative intensity of each peak is different, the diffraction patterns of the three complexes are similar wherein a strong peak at ca. 11.7° is present in all the complexes but not in pure β -CD. β -CD/PPG IC has been shown to possess a columnar structure.^{5,8} Therefore, a columnar structure is also apparent for the two β -CD/F-oligomer ICs.

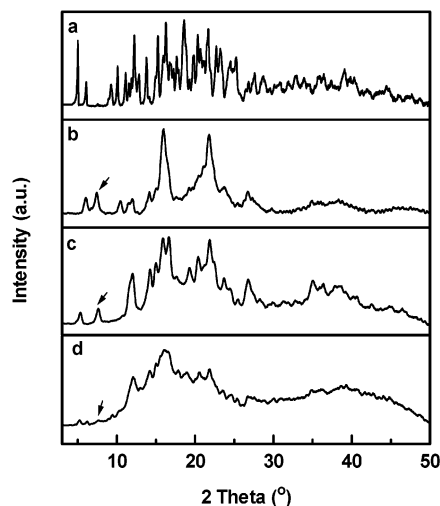


Figure 3. X-ray diffraction patterns for γ -CD (a), γ -CD/PPG IC (b), γ -CD/F-1 IC (c), and γ -CD/F-4 IC (d).

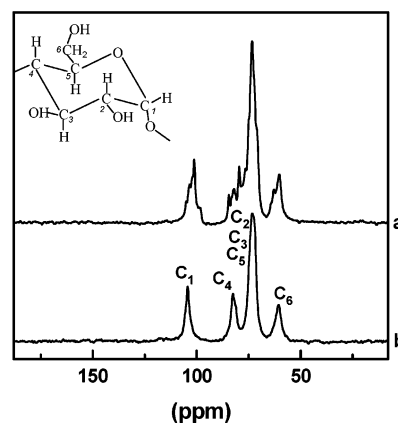


Figure 4. ^{13}C CP/MAS NMR spectra of γ -CD (a) and γ -CD/F-1 (b).

Figure 3 shows the XRD patterns of γ -CD, γ -CD/PPG IC, and two γ -CD/F-oligomer ICs. The XRD patterns of the γ -CD/F-oligomer ICs are similar to those of the γ -CD/PPG IC and other polymer/ γ -CD complexes.^{10,11} Furthermore, the fingerprint peak for the columnar structure of γ -CD-IC at ca. 8.0° is present in all these complex. Thus, a columnar structure is also expected in γ -CD/F-oligomer ICs.

Figure 4 shows the ^{13}C CP/MAS NMR spectra of γ -CD and γ -CD/F-1 IC. The spectrum of γ -CD shows resolved carbon resonances from each of the glucose units while the spectra of ICs show unresolved carbon resonances. This result indicates that CD adopts a symmetrical cyclic conformation in the ICs due to the inclusion of polymer chain while pure CD crystal assumes a less symmetrical conformation. Thus, the formation of the inclusion complexes in the present study is further supported by the ^{13}C CP/MAS NMR measurements.

Figure 5 shows the FTIR spectra of pure γ -CD, the CD/F-oligomer ICs, and the pure oligomers. The spectra of γ -CD and ICs were recorded at 120°C to exclude moisture. The spectra of ICs are similar to those of pure CDs in the range of 4000 – 1500 cm^{-1} over which the pure oligomers have no absorbance. F-oligomers have strong absorbance over the frequency range of 1400 – 1000 cm^{-1} . The peak at 1208 cm^{-1} in F-1/F-2 or at 1240 cm^{-1} in F-3/F-4 moves to 1229 and 1244 cm^{-1} in the respective ICs. Such a movement can be clearly seen in

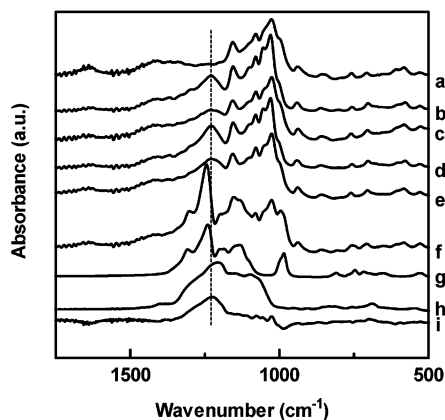


Figure 5. FTIR spectra of γ -CD (a), β -CD/F-1 IC (b), γ -CD/F-1 IC (c), β -CD/F-2 IC (d), γ -CD/F-2 IC (e), γ -CD/F-3 IC (f), F-3 (g), F-2 (h), and difference of (e) – (a) (i).

the difference spectrum (spectrum i in Figure 5). In the difference spectrum, it is also apparent that the relative intensity of the shoulder peak at ca. 1100 cm^{-1} in pure F-2 is attenuated. Since both the change of the conformation of polymer chains and the presence of interpolymer interaction can cause changes of the C–F stretching bands,³³ the inclusion of the perfluorinated oligomer chains in the narrow CD channels is likely to have led to the observed changes in the FTIR spectra.

Conclusions

The inclusion complexation behavior of perfluorinated oligomers with cyclodextrin is different from that of their corresponding hydrogenated analogues. Oligo-(tetrafluoroethylene oxide-*co*-difluoromethylene oxide) forms ICs with β -CD and γ -CD but not with α -CD, while oligo(hexafluoropropylene oxide) only forms ICs with γ -CD. XRD studies demonstrate that all the ICs are crystalline and possess a columnar structure. ^{13}C CP/MAS NMR spectra of the ICs indicate that CDs adopt a more symmetrical conformation in the complex, while pure CD assumes a less symmetrical conformation in the crystal state. FTIR studies demonstrate the presence of F-oligomer and CD in the ICs. A molecular modeling study is in progress, aiming to better understand the complexation behavior of the perfluorinated oligomers with CD.

Acknowledgment. We thank the National University of Singapore for its financial support of this research and Ms. Liu for assistance in XPS measurements.

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MA034260N