

Understanding the Microstructure of β -cyclodextrin Polymers with Solid State Fluorine NMR

Xiao, L. and Dichtel, W.R. (Northwestern U., Chemistry)

Introduction

We recently reported a β -cyclodextrin (β -CD)-based polymer network with high affinity for perfluorooctanoic acid (PFOA). The β -CD polymer DFB-CDP reduces PFOA concentrations from $1 \mu\text{g L}^{-1}$ to $<10 \text{ ng L}^{-1}$, at least 7 times lower than the 2016 U.S. EPA advisory level (70 ng L^{-1}).¹ Since DFB-CDP is an amorphous crosslinked polymer, limited characterization techniques can be applied to understand the structure of the polymers. Considering that the crosslinker DFB is perfluoroarene, detecting fluorines in solid state ^{19}F MAS NMR will enhance our understanding on the polymers' microstructure drastically.

Experimental

Solid state 600 MHz NMR equipped with 89 mm bore, 14 T #2 magnet was used to conduct 1D ^{19}F MAS NMR analysis. The spinning rate was 48 kHz while number of scans was 1024.

Results and Discussion

^{19}F MAS NMR spectrum of **DFB-CDP-3-As synthesized** exhibited two broad peaks at -142.4 and -159.2 ppm (Fig. 1A). These chemical shifts are similar to those found in the ^{19}F NMR spectrum of model compound **2a** obtained in solution ($\delta = -142.9$ and -159.0 ppm). This observation indicates that the DFB-CDP polymers are linked mostly by 4,4'-disubstituted decafluorobiphenyl groups. The spectrum of **DFB-CDP-3-As synthesized** also exhibits a shoulder around -164.0 ppm, which corresponds to the fluorines adjacent to the phenol in the neutral form of **2b** (**2b'**, $\delta = -163.3$ ppm). Upon treatment of **DFB-CDP-3-As synthesized** with K_2CO_3 to deprotonate the as-synthesized polymer, the chemical shifts of the shoulder shifted to -172.4 ppm, and a similar shift was observed in the solution spectrum of **2b** upon deprotonation ($\delta = -171.0$ ppm). These observations suggest that the shoulder peak corresponds to fluorines on phenolated aryl rings that are incorporated into **DFB-CDP-3**. Notably, the shoulder at -172.4 ppm is much less prominent in the less-phenolated **DFB-CDP-1-Deprotonated** (Fig. 1B), which is consistent with the phenolate loadings determined by other methods.²

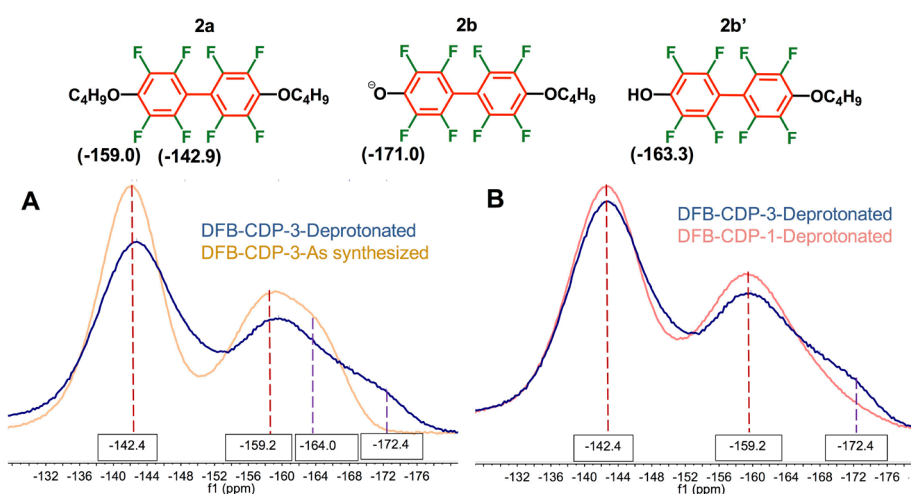


Fig.1 ^{19}F MAS NMR of DFB-CDPs at 600 MHz while spinning at 48 kHz. A. ^{19}F MAS NMR of as-synthesized and deprotonated DFB-CDP-3. Orange trace: As-synthesized DFB-CDP-3; Blue trace: DFB-CDP-3-Deprotonated; B. ^{19}F MAS NMR of deprotonated DFB-CDPs. Red trace: DFB-CDP-1-Deprotonated; Blue trace: DFB-CDP-3-Deprotonated.

Conclusions

^{19}F MAS NMR proves the substitution pattern of DFB incorporated into the polymer network, the presence and relative concentrations of phenolates in the polymers were also confirmed.

Acknowledgements

The National High Magnetic Field Laboratory is supported by the National Science Foundation through NSF/DMR-1157490/1644779 and the State of Florida. This research was also supported by NSF through the Center for Sustainable Polymers (CHE-1413862) and by the Strategic Environmental Research and Development Program (ER18-1026).

References

- [1] Xiao, L., *et al.*, J. Am. Chem. Soc, **139**, 7689-7692 (2017).
- [2] Xiao, L., *et al.*, Manuscript in preparation.