

Structure and Dynamics of Perfluoroalkanes and Their β -Cyclodextrin Inclusion Compounds Investigated by Solid-state ^{19}F MAS NMR

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Introduction

Perfluoropolymers such as poly(tetrafluoroethylene) (PTFE) are high performance and functional materials that exhibit a variety of outstanding properties such as chemical resistance, low surface tension, low dielectric constant and low refractive indices. Despite such invaluable advantages, the applications of perfluoropolymers to blends or composites are less advanced due to their incompatibility with unfluorinated materials. As an effective and facile approach, we focused on cyclodextrin (CD) as an inclusion host that is capable of including polymers as well as small molecules in their hydrophobic cavities. In fact, we have recently found that perfluoroalkanes (PFAs), those are model compounds of PTFE, form solid-state inclusion compounds (ICs) with β -CD [1]. Meanwhile, several works on the molecular structure and dynamics of both CDs and guest polymers have been reported using solid-state $^1\text{H}\rightarrow^{13}\text{C}$ cross polarization (CP) / magic angle spinning (MAS) NMR [2]. In the present work, we investigated the molecular structure and dynamics of PFAs in β -CD ICs using solid state ^{19}F MAS and $^1\text{H}\rightarrow^{19}\text{F}$ CP/MAS NMR spectroscopy with the aid of thermal analyses, infrared (IR) spectroscopy, and X-ray diffraction method.

Experimental

Inclusion compounds (ICs) consisting of *n*-perfluorononane (*n*- C_9F_{20}) and β -CD (abbreviated as $\text{C}_9\text{F}_{20}/\beta$ -CD) was prepared by vigorous stirring of C_9F_{20} with saturated aqueous solution of β -CD. The obtained precipitate was washed by water to remove unreacted C_9F_{20} and β -CD and then dried under vacuum. $\text{C}_{20}\text{F}_{42}/\beta$ -CD IC was also prepared in a similar manner. Solid-state ^{19}F NMR measurements were performed between -40 and 120°C at a MAS rate of 15 kHz .

Results and discussion

The elemental analyses indicate that the molar ratio of C_9F_{20} to β -CD in $\text{C}_9\text{F}_{20}/\beta$ -CD is 1:2, while that of $\text{C}_{20}\text{F}_{42}$ to β -CD in $\text{C}_{20}\text{F}_{42}/\beta$ -CD is approximately 1:4. Both the ratios are reasonable from the view of the molecular sizes estimated by quantum chemical calculations. For each IC, specific IR absorption band associated with the vibrations along the longer axis of PFAs were weakened with the inclusion by β -CD, suggesting that the inclusion may give rise to certain conformational changes in PFAs (figures are not shown).

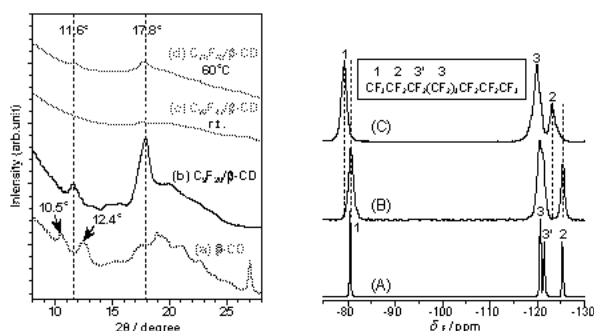


Figure 1. (Left) WAXD patterns of (a) β -CD, (b) $\text{C}_9\text{F}_{20}/\beta$ -CD, and (c, d) $\text{C}_{20}\text{F}_{42}/\beta$ -CD. (a) to (c) were obtained at room temperature while (d) was at 60°C . (Right) ^{19}F NMR spectra of $\text{C}_9\text{F}_{20}/\beta$ -CD (A) and neat C_9F_{20} (B) at -35°C and that at 20°C (C).

The WAXD patterns shown in Figure 1 (Left) suggest that $\text{C}_9\text{F}_{20}/\beta$ -CD forms a channel-type crystal at room temperature, while $\text{C}_{20}\text{F}_{42}/\beta$ -CD is nearly amorphous. The ^{19}F direct polarization (DP)

MAS NMR signals for $\text{C}_9\text{F}_{20}/\beta$ -CD IC resonate at higher frequencies by 1.4–2.3 ppm than those for neat C_9F_{20} (Figure 1, Right). The high-frequency shift is also observed for $\text{C}_{20}\text{F}_{42}/\beta$ -CD. These changes in chemical shift can be predominantly caused by the less dielectric environment in the β -CD cavities. When $\text{C}_9\text{F}_{20}/\beta$ -CD is heated, new ^{19}F signals are observed at lower frequencies than the signals observed at low temperatures. By analogy with the chemical shifts of isolated C_9F_{20} , they can be assigned to the fluorines in the uncovered part of C_9F_{20} . The $^1\text{H}\rightarrow^{19}\text{F}$ CP/MAS NMR spectrum of $\text{C}_9\text{F}_{20}/\beta$ -CD observed at 120°C is shown in Figure 2 (Left, red line), in which fluorines located at relatively immobile sites or in components close to protons are preferentially observed [3]. Since the newly appearing signals (pointed by arrows) are weakened in the CP/MAS spectrum (green line), they can be ascribed to the fluorines distant from hydrogens of β -CD or indeed those in the part coming out of the β -CD host. However, PFAs confined in β -CD channel hardly evaporate or degrade unless the host is pyrolytically decomposed above 300°C as demonstrated by thermo-gravimetric analysis (TGA). As estimated from the ^{19}F peak area, the uncovered C_9F_{20} reaches approximately 60% of the total amount at 120°C , while the other part still stays in the β -CD channel.

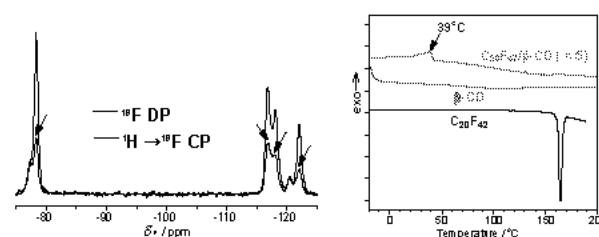


Figure 2. (Left) ^{19}F DP MAS and $^1\text{H}\rightarrow^{19}\text{F}$ CP/MAS NMR spectra of $\text{C}_9\text{F}_{20}/\beta$ -CD at 120°C with a contact time of 0.1 ms. (Right) DSC curves for $\text{C}_{20}\text{F}_{42}$, β -CD, and $\text{C}_{20}\text{F}_{42}/\beta$ -CD.

On the other hand, ^{19}F NMR signals for $\text{C}_{20}\text{F}_{42}/\beta$ -CD do not show significant changes in the measurement temperature range. However, the differential scanning calorimetry (DSC) curve of $\text{C}_{20}\text{F}_{42}/\beta$ -CD gives an exothermic peak at ca. 40°C (Figure 2, Right), suggesting that β -CD molecules rearrange to form more ordered structures. Actually, thermal treatment of $\text{C}_{20}\text{F}_{42}/\beta$ -CD at 60°C for several hours leads to channel-type crystallites similar to $\text{C}_9\text{F}_{20}/\beta$ -CD (Figure 1, Left). For both ICs, the structural changes caused by heating are reversible but time-consuming, which are due to the hydration and dehydration processes of crystal water that are deeply involved in the IC formation.

The ^{19}F spin-lattice relaxation times in the laboratory frame (T_1^{F}) for the fluorines of neat PFAs are different from each other, while those of PFA/ β -CD ICs are similar at every temperature. This is because librational motion of C–F bond is effectively suppressed in the β -CD channel, and thereby ^{19}F spin diffusion effectively occurs. The T_1^{F} values for PFA/ β -CD ICs are smaller than those for the corresponding PFAs, indicating that the internal rotation of $-\text{CF}_3$ is on the Larmor timescale in the β -CD channel. The ^{19}F spin-lattice relaxation times in the rotating frame ($T_1^{\text{F}_s}$) for fluorines of PFA/ β -CD ICs are very long, suggesting that the PFAs undergo no motions around ca. 100 kHz such as conformational changes and/or overall rotation along the molecular axis even in the β -CD channel.

Conclusions

For $\text{C}_9\text{F}_{20}/\beta$ -CD IC, approximately 60% of C_9F_{20} guests may come out of the β -CD channel around 120°C , but they scarcely evaporate unless the IC decomposes. In contrast, most of $\text{C}_{20}\text{F}_{42}$ molecules cannot be uncovered even at 120°C , but $\text{C}_{20}\text{F}_{42}/\beta$ -CD commences rearrangements above 40°C , which leads to more ordered structures. In β -CD channel, PFA molecules undergo reduced libration at C–F bonds but vigorous rotation at the terminal $-\text{CF}_3$.

References

- [1] Tatsuno, H.; Ando, S. *to be submitted*.
- [2] Lu, J.; Mirau, P. A.; Tonelli, A. E. *Prog. Polym. Sci.* **2002**, *27*, 357-401.
- [3] Ando, S.; Harris, R. K.; Reinsberg, S. A. *Magn. Reson. Chem.* **2002**, *40*, 97-106.