Hydrogen Bonded Self-Assembly of Pyridine Terminated Oligoketones

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Helix is one of the most intriguing structures readily observed in nature as in the cases of DNA, proteins, and even synthetic polymers. We have recently reported that aliphatic polyketones composed of 3,3-dimethylpentane-2,4-dione spontaneously adopt helical conformations for oligomers longer than tetramer.[1] These findings prompted us to construct larger molecular assemblies using polyketone helices as components. In this research, we investigated hydrogen-bond-driven self-assembly of 3-acylaminopyridine-terminated polyketones **1**–**3**.

Polyketone analogs **1**–**3** (**Fig. 1a**) with varying chain lengths bearing a hydrogen-bonding part at each end were prepared by amidation of corresponding acid chlorides with 3-aminopyridine. Single crystals of the shortest chain **1** obtained by recrystallization from nitromethane showed a hydrogen bonded 3-dimensional network constructed by NH•••N(pyridine) hydrogen bonds. While **1** in crystal did not adopt helical conformation (**Fig. 1b**), the crystal structure of **2** showed infinite chains in which polyketones of *P*- and *M*-handed helical conformations were alternatively connected by hydrogen bonds (**Fig. 1c**). Variable temperature ^{1}H NMR of **2** in $CDCl_3$ (75 mM) showed significant down-field shift (from 8.48 to 9.11 ppm) of amide protons upon cooling to –40 ºC, suggesting the formation of similar chains in solution. When 50 mM chloroform solutions of **1–3** were cooled to –20 °C, only the solution of **3** exhibited gelation while those for **2** and **4** did not. This suggests that the closed oligoketone channel observed in the solid-state for **3** is plausibly maintained even in the solution-state.

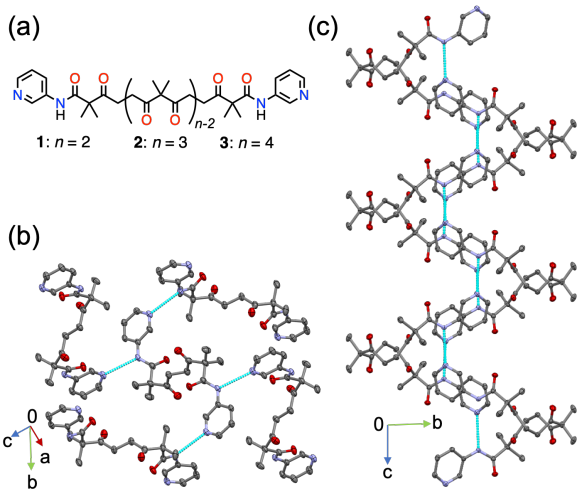

Fig. 1 (a) Chemical structures of 3-acylaminopyridine-terminated polyketones **1**-**3**. Crystal structure representations of (b) **1** and (c) **2**, illustrating intermolecular H-bonding [blue dotted lines indicate NH•••N(pyridine) bonds].

1) Y. Ide, Y. Manabe, Y. Inaba, Y. Kinoshita, J. Pirillo, Y. Hijikata, T. Yoneda, K. I. Shivakumar, S. Tanaka, H. Asakawa, Y. Inokuma, *Chem. Sci.* **2022**, *13*, 9848.

