Synthesis of Monodisperse Polyketones and Chain Length Dependent Crystallinity Changes

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Monodisperse oligomers enables to elucidate the precise correlations of their structure and molecular weights in comparison with the corresponding polydisperse polymers.[1] Here we report the synthesis of monodisperse aliphatic polyketones up to 20 mer and revealed their chain length dependent crystallinity changes.

Monodisperse aliphatic polyketones up to **10 mer** were iteratively synthesized by repeating terminal-selective silylation and subsequent silver(I) oxide mediated homo- or cross-coupling reactions from an acetylacetone derivative as a monomer.[2] Further longer polyketones **12, 16** and **20 mer** were obtained by polymerization reaction of bis-silylated tetramer[1] and preparative recycling GPC separation in 7%, 6%, and 5% yields, respectively (**Figure 1a**).

The crystallinity transition of the aliphatic polyketones upon their chain length elongation was investigated by single- and powder X-ray diffraction analysis. While polyketones until **4 mer** have their own conformations in the single crystal structures[2], the conformations above **5 mer** were estimated to be converged into the helical conformation (**Figure 1b**). This crystallinity changes were estimated by comparing the powder X-ray patterns of polyketones with the calculated crystal structure of the polyketones.

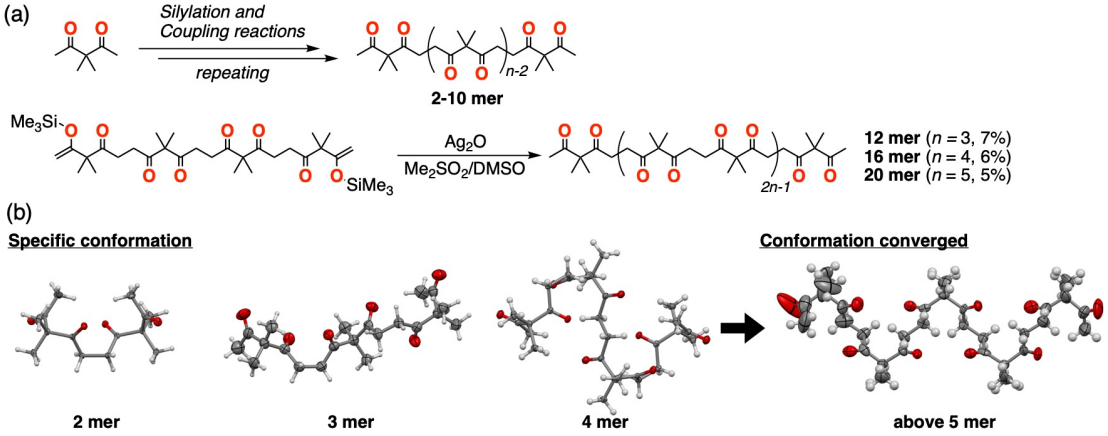

Figure 1. (a) Synthesis of monodisperse aliphatic polyketones **2-10**, **12, 16, and 20 mer**; (b) Chain length dependent crystal structure transitions of the polyketones.

1) S. Binauld, D. Damiron, L. A. Connal, C. J. Hawker, E. Drockenmuller, *Macromol. Rapid Commun.*, **2011**, *32*, 147; 2) (a) M. Uesaka, Y. Saito, S. Yoshioka, Y. Domoto, M. Fujita, Y. Inokuma, *Commun. Chem.*, **2018**, *1*, 23; (b) Y. Manabe, M. Uesaka, T. Yoneda, Y. Inokuma, *J. Org. Chem.*, **2019**, *84*, 9957.