Synthesis of Chiral Guanidine Multimer by Addition Reaction of Diamine and Biscarbodiimide

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Polyaddition reaction is a stepwise polymerization and its reaction behavior basically follows the classical theory of polycondensation.[1,2] Herein we present an exception that deviates considerably from the common perception. Optically active *trans*-4a,8a-decahydroquinoxaline, (*S*,*S*)-**1**, and 1,4-phenylenebis(arylcarbodiimide)s **2** react instantly with each other under ambient and non-equimolar conditions with **1** in a few excess, giving the corresponding 2:1 adduct, **1-2-1**, without predicted molecular weight distribution. The **1-2-1** can be extended in stages to **1-(2-1)$_3$** followed by **1-(2-1)$_7$** by repeating the treatment with just a half molar of **2** without requiring any activation, protection, or laborious purification, which are "living" molecular chains containing an amino group at both ends and sequenced guanidines in the main chain. End-capping of these telechelic molecules can derive a new class of chiral oligoguanidines with a controlled length (Figure 1, lower left), while an equimolar mixing of **1** and **2** can provide facile access to chiral polyguanidines ($M_w \approx 20{,}000$, Figure 1, upper). This study not only provides the first polyaddition between chiral diamines and biscarbodiimides but also opens up a new avenue to designing highly functionalized molecular chains and investigating the chain-length dependence of their properties and functions such as self-diffusion coefficient *D* (Figure 1, lower right), absorption, circular dichroism, and asymmetric catalysis.

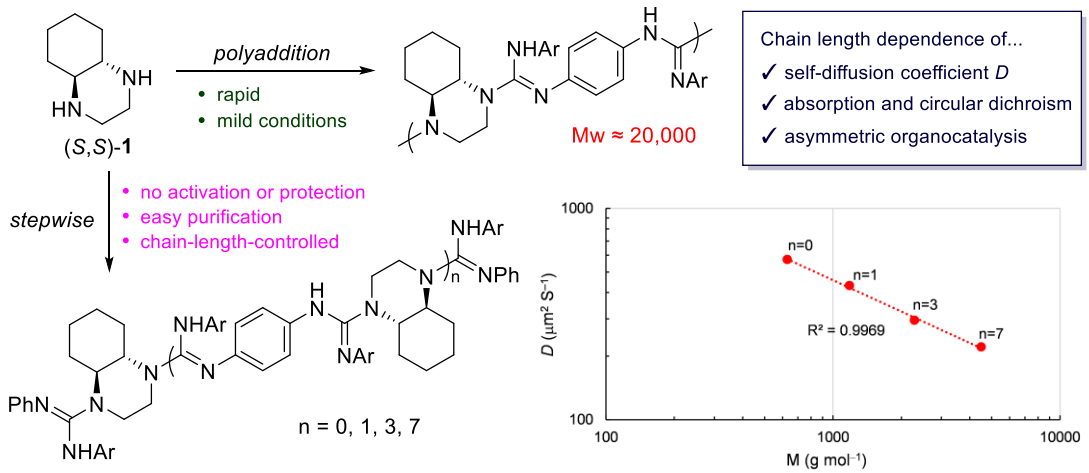

Figure 1. Graphical abstract of this study (Ar = 1-naphthyl).

1) P. J. Flory, *J. Am. Chem. Soc.* **1936**, *58*, 1877–1885.
2) L. H. Peebles, *Macromolecules* **1974**, *7*, 872–882.