Synthesis of Cyclic or Linear Diblock Copolypeptoids and their Self-assembly in Solution

N-Heterocyclic carbene (NHC)-mediated ring-opening polymerization of N-decyl-N-carboxyanhydrides (De-NCA) were shown to occur in a controlled manner, yielding cyclic poly(N-decylglycine)s (c-PNDGs) with polymer molecular weights (MW) between 4.8 and 31 kD and narrow molecular weight distributions (PDI < 1.15). The reaction exhibits pseudo-first order kinetics with respect to monomer concentration. The polymer MW increases linearly with conversion, consistent with a living polymerization. ESI MS and SEC analyses confirm the cyclic architectures of the forming polymers. DSC and WAXS studies reveal that the c-PNDG homopolymers are highly crystalline with two prominent first-order transitions at 72-79 °C and 166-177 °C. A series of amphiphilic cyclic diblock copolypeptoids [i.e., poly(N-methylglycine)-b-poly(N-decylglycine) (c-PNMG-b-PNDG)] with variable molecular weight and composition were synthesized by sequential NHC-mediated polymerization of the corresponding N-methyl-N-carboxyanhydride (Me-NCA) and De-NCA monomers. 1H NMR analysis reveals that adjusting the initial monomer to NHC molar ratio can readily control the block copolymer chain length and composition. The solution self-assembly of the copolypeptoids have been investigated.

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The solution self-assembly of the copolypeptoids have been investigated. Time-lapsed light scattering and cryogenic transmission electron microscopy (cryo-TEM) analyses of c-PNDG-b-PNMG samples showed that the amphiphilic cyclic block copolypeptoids self-assemble into spherical micelles that reorganize into micrometer-long cylindrical micelles with uniform diameter in room temperature methanol over the course of several days. An identical morphological transition has also been noted for the linear analogues, which occurs more rapidly than for the cyclic copolypeptoids. We tentatively attribute this difference to the different crystallization kinetics of the solvophobic block (i.e., PNDG) in the cyclic and linear block copolypeptoids.


Fig. Representative cryo-TEM images obtained from dilute methanol solutions of the cyclic PNMG\textsubscript{105}-b-PNDG\textsubscript{16} block copolypeptoid after 1 h (A), 2 h (B), and 15 d (C), and the linear PNMG\textsubscript{112}-b-PNDG\textsubscript{16} block copolypeptoid after 1 h (D), 2 h (E), and 7 d (F) in methanol.