Preparation of crystalline nanostructured materials by self-assembly of cage siloxanes modified with a long-chain alkyl group and silanol groups

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【Introduction】 Cage siloxanes with rigid polyhedral structures are useful as building blocks for nanostructured siloxane-based materials. Various mesostructures such as lamellar and two-dimensional hexagonal structures have been obtained by self-assembly of amphiphilic double-4-ring (D4R)-type cage siloxanes modified with long alkyl groups.[1)] Recently, we reported the formation of hydrogen-bonded molecular crystals of cage siloxanes modified with dimethylsilanol ($SiMe_2OH$) groups.[2,3)] In this study, we report the formation of mesostructured materials with crystalline frameworks by self-assembly of an amphiphilic D4R siloxane modified with a long-chain alkyl group and seven $SiMe_2OH$ groups.

【Experimental】 The D4R-type siloxane modified with a $SiMe_2C_{18}H_{37}$ group and seven $SiMe_2OH$ groups (**C18D4R-DMS**) was prepared by stepwise silylation of D4R silicate anions ($Si_8O_{20}^{8-}$) with chlorodimethylsilane and chlorodimethyloctadecylsilane, followed by conversion of the $SiMe_2H$ groups into the $SiMe_2OH$ groups, according to our previous report[4)] with some modifications to improve the purity. The molecular crystals of **C18D4R-DMS** were obtained by evaporation of the diethyl ether solution after the addition of H_2O.

【Results and discussion】 The synthesis of **C18D4R-DMS** with relatively high purity was confirmed by FT-IR, NMR, and MALDI-TOF MS analyses. ^{29}Si MAS NMR spectrum of the molecular crystals showed that the molecular structure of **C18D4R-DMS** was retained in the crystals (Fig. 1a). The XRD pattern of the crystals showed many sharp peaks, and the strongest peak at the lowest angle (d = 3.7 nm) with second- and third-order peaks suggested the formation of a mesostructure (Fig. 1b). Other peaks at higher angles can be ascribed to the molecular arrangement of the cage siloxanes.

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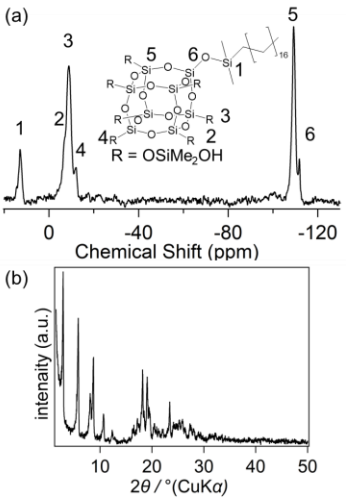

Fig. 1 (a) ^{29}Si MAS NMR spectrum and (b) XRD pattern of **C18D4R-DMS**.