replacing MAR16-2015-005470.

for the MAR16 Meeting of
The American Physical Society

Pore Diameter Dependence and Segmental Dynamics of Poly-Z-L-lysine and Poly-L-alanine Confined in 1D Nanocylindrical Geometry

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Structure formation, thermodynamic stability, phase and dynamic behaviors of polypeptides are strongly affected by confinement. Since understanding the changes in these behaviors will allow their rational design as functional devices with tunable properties, herein we investigated Poly-Z-L-lysine (PZLL) and Poly-L-alanine (PAla) homopolypeptides confined in nanoporous alumina containing aligned cylindrical nanopores as a function of pore size by differential scanning calorimetry (DSC), Fourier Transform Infrared Spectroscopy, Solid-state NMR, X-ray diffraction, Dielectric spectroscopy(DS). Bulk PZLL exhibits a glass transition temperature ($\mathrm{T_g}$) at about 301K while PZLL nanorods showed slightly lower $\mathrm{T_g}$ (294K). The dynamic investigation by DS also revealed a decrease (4K) in $\mathrm{T_g}$ between bulk and PZLL nanorods. DS is a very sensitive probe of the local and global secondary structure relaxation through the large dipole to study effect of confinement. The results revealed that the local segmental dynamics, associated with broken hydrogen bonds, and segmental dynamics speed-up on confinement.

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Date submitted: 06 Nov 2015 Electronic form version 1.4