"Nanochemistry and biotechnology"

The effect of solvent and time on morphology of PEO/PCL block copolymer micelles

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The micellization of MOPEO-*b*-PCL diblock and PCL-*b*-PEO-*b*-PCL triblock copolymers (DBC and TBC) based on methoxypoly(ethylene oxide) (M_n=2.5 and 4.5 kDa) or poly(ethylene oxide) (M_n=6 kDa) and poly(ε-caprolactone) with variable M_n, and also the micelle morphology in dilute water/dioxane and aqueous solutions were studied using static and dynamic light scattering and TEM. The increase in thermodynamic stability and average size of DBC micelles at the lengthening either the "core"-forming PCL blocks or the "corona"-forming MOPEO blocks has been established. The micelles of TBC showed the smallest stability and average size. Amphiphilic DBC and TBC macromolecules formed in the mixed solvent small (3-14 nm) classical and "flower"-like micelles of a spherical shape and small fractal aggregates caused by the "coronas" interactions (Fig. 1 **a**, **b**). This self-assembly by micellar "coronas" developed in pure water (after dialysis of initial water/dioxane solutions) and in time, thus resulting in the appearance of large fractal spherical, elongated and "rod"-like structures, in which there was no common hydrophobic "core". The reasons for such phenomena are discussed.

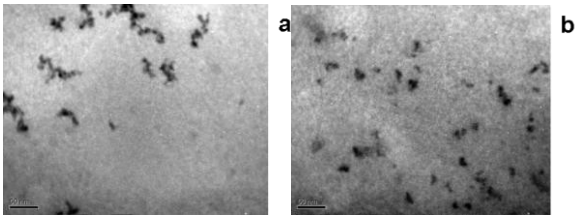

Fig. 1. TEM images for DBC (**a**) and TBC (**b**) micelles and their small fractal aggregates in water/dioxane (70/30 v/v) mixture. C=0.3 kg·m^{-3}.