Block Copolymer Micelles as Nanocontainers for Controlled Release of Proteins from Biocompatible Oil Phases

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SUPPORTING INFORMATION

As described in the article, the total dry-state volume of PCL-*b*-P2VP micelles spin-cast on silicon from toluene can be calculated from AFM images by approximating the micelles as spherical caps. The volume of P2VP is the total micelle volume multiplied by the weight fraction of P2VP in the polymer (based on number average MW) assuming equal densities of PCL and P2VP. Next, the diameter of the P2VP core can be computed for the polymer in solution assuming a spherical geometry and no solvation. The corona thickness, δ, can be determined by subtracting the core radius from the overall micelles radius determined by dynamic light scattering. Knowing the corona thickness, we can compare the conformation of the corona chains to that of a fully extended chain and to the expected end-to-end distance for a PCL chain. The fully extended chain length ($nl\cos\theta$) for PCL is 269 nm for M_n = 35 400. The expected root mean square (RMS) end-to-end distance for PCL chains is obtained using the characteristic ratio (C_∞) and an estimated expansion factor (α) in toluene:

$$(1)\ \langle r^2\rangle^{1/2} = (\alpha^2 C_\infty n l^2)^{1/2}$$

The theta temperature for PCL in toluene[1] is 15 °C, so we expect α to be greater than, but close to unity. The characteristic ratio of PCL[2, 3] is ~6. We used a number-weighted average value of the C-O and O-O bond lengths for l to obtain a value for $\langle r^2\rangle^{1/2}$ of 17.2 nm.

The fractional chain extension ($\delta / nl\cos\theta$) of polymer blocks making up the micelle corona depends on a variety of factors including the composition ratio of the core and corona blocks, size of the micelle core, micelle aggregation number, length of the corona chains as well as the chemical nature of the corona chains and solvent quality.[4, 5] Fractional chain extensions have been observed ranging from 20 to 100%.[4-12] Here, the PCL corona thickness is 24% of the fully extended chain length (Table 1). The PCL chains in our micelles are long (310 repeat units with 7 bonds per repeat unit along the backbone) compared to the average micelle corona chain lengths. Because the PCL chains are long compared to the P2VP chains, the micelles are 'hairy' micelles, as opposed to 'crew-cut' micelles and the former are generally characterized by lower corona chain extensions.[4, 5] Charged polymer chains result in more extended conformation because of electrostatic repulsion of like charges on adjacent chains. PCL is uncharged so we expect lower chain extension as observed. Our results agree well with a similar long chain, uncharged micelle system of PS-*b*-PI in decane studied by McConnell et al.[7] who observed corona chains that were 21%-35% of the fully extended chain length (calculations done by Zhang et al.[4])

The calculated corona thickness is four times the expected RMS end-to-end distance. Steric effects near the core/corona interface cause the chain to take on a more extended conformation compared to the expected end-to-end distance. This has been observed by others[4-12] including Schillen et al.[9] who observed chain lengths longer than the RMS end-to-end distance (calculated assuming α = 1) for PI-*b*-PMMA in acetonitrile even at 20 °C below the theta temperature, which should promote compact corona chains (α < 1).

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