Title: Self-assembly behavior of functional polycaprolactones

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Abstract

Amphiphilic homo polycaprolactones (PCLs) having di-, tri-, tetra(ethylene glycol) (ME_2, ME_3, ME_4) mono functional groups and a tri(ethylene glycol)/dodecyl (ME_3DD) di functional group were synthesized by ring opening polymerization (ROP) of the corresponding γ-functionalized ε-caprolactone (CL) monomers. All the homopolymers formed spherical micelles in aqueous media with variable sizes between 73.2 nm-152.0 nm. The critical micelle concentration (CMC) for PME_2CL, PME_3CL, PME_4CL, and PME_3DDCL were 2.2×10^{-1}, 2.4×10^{-1}, 3.7×10^{-1} gL^{-1}, and 1.8×10^{-2} gL^{-1}, respectively. With the increasing of hydrophilic oligo(ethylene glyco) chain length, the polymeric micelles became less stable and their cloud point tempeature increased from 58.6 ^{o}C–85.8 ^{o}C. PME_3DDCL micelles were more stable due to the increased hydrophobicity from the additonal dodecyl functional group and had the highest loading capacity of 4.8%. However, it significantly affected the cloud point tempeature (T_{cp}) of PME_3DDCL which was not detected even lowing temperature to 4 ^{o}C. Compared with homopolymers, amphiphilic blcok copolymers tend to have higher thermodynamic stability. Therefore, a new amphiphilic diblcok copolymer polycaprolatone-block-poly(triethylene glyco/propyl-di-substituted caprolacotne) (PCL_{44}-*b*-$P(ME_3PyCL)_{56}$) with a mocelular weight of 5,300 g/mol and a PDI of 1.69 was preparared by sequential polymerization. The self-assembly was achieved in aqueous media and the CMC was 2.41×10^{-3} gL^{-1}. It is comparable to that (1.54×10^{-3} gL^{-1}) of polycaprolactone-block-poly(triethylene glycol) (PCL_{48}-*b*-$P(ME_3)_{52}$) diblock copolymer with a molecular weight of 6,000 g/mol and a PDI of 1.38.