SYNTHESIS OF SURFACTANT-FREE AMPHIPHILIC JANUS NANOPARTICLES AND THEIR APPLICATION IN PICKERING EMULSION POLYMERIZATION

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The use of amphiphilic Janus nanoparticles (JNPs) in applications such as Pickering emulsions or surface functionalization, can be attractive, especially when the use of molecular surfactants is not desired. Furthermore, the JNPs have significant advantages over the homogeneous nanoparticles (HNPs) especially with respect to the ability to precisely tune their surface polarity, by tuning the aspect ratio of the polar vs. non-polar lobes. The main challenges in employing these solid-state amphiphiles are: synthesis in surfactants free conditions and scalability of the synthetic methods. Here we present a scalable synthetic method for obtaining polymeric JNPs in surfactant-free conditions starting from crosslinked polystyrene (PS) seed nanoparticles on which we grew lobes of different sizes via seeded emulsion polymerization of 3-(triethoxysilyl)propyl-methacrylate (3-TSPM) monomer.[1] The homologous series of JNP amphiphiles resembles that of a surfactant series with varying hydrophilic-liophilic balance (HLB). In order to further demonstrate the capability of this next generation of amphiphiles we employ the JNP series in the emulsification of oils (solvents and monomers) of varying polarity in water. Depending on the polarity of the JNPs o/w or w/o emulsions are obtained. From the catastrophic and transitional emulsions phase transitions curves we were able to calculate the interfacial energy of the JNPs with oils and water. Here we demonstrate that the HLB balance and polarity of the JNPs can be tuned, such that polarity inversion within the JNP homologous series is obtained. The homologous series of JNPs was also successfully employed in Pickering emulsion polymerization of styrene and methylmetacrylate monomers creating colloidosomes and hollow polymeric structures with nanostructured surfaces.

[1] Wu, D.; Chew, J. W.; Honciuc, A. Polarity Reversal in Homologous Series of Surfactant-Free Janus Nanoparticles: Toward the Next Generation of Amphiphiles. *Langmuir* **2016**, *32* (25), 6376–6386.

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