Surface Energy of Janus Nanoparticles and Their Application in Pickering Emulsions Polymerization

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Surface energy of nanoparticles is an important physicochemical parameter because it controls the colloid stability, surface adhesion, flowing ability, aggregation, etc. However, direct measurement of the surface energy of nanoparticles is not as easy as for bulk materials. Currently, the common method for measuring surface energy of particles is by measuring the contact angle *via* Washburn method. But this method has significant drawbacks, while it works relatively well for micro-particles, it often fails in the nano-range, due to packing reproducibility and limited solvent intake by the nano-capillaries.

Alternatively, we propose a new method to measure the interfacial energy of nanoparticles. For this we have synthesized a homologous series of varying polarity Janus nanoparticles (JNPs) consisting of a hydrophobic polystyrene (PS) lobe and more polar P(3-TSPM) lobe by surfactant-free seeded emulsion polymerization. In this case the P(3-TSPM) lobe is more polar than the PS lobe due to the presence of polar -OH functional groups on its surface. The size of the PS lobe was kept constant, while that of the P(3-TSPM) lobe was changed, thus the overall particle polarity of the surface also changed systematically in the homologous series.

Next, we employed the homologous series of JNPs to emulsify several oils, with varying polarity, such as heptane, toluene, styrene, dichloromethane and methyl methacrylate in water. In the phase diagram of oil-to-water ratio vs. JNP lobe size both transitional and catastrophic emulsion phase inversions from o/w to w/o could be observed. From the evolution of these phase transition lines with different polarity oils we were able to calculate the relative interfacial energy of each JNP with water and oil.

The relative interfacial energy of JNPs with water decreased by 92% and increased by 100% with respect to heptane in the homologous series. The obtained result clearly demonstrates that the polarity of JNPs significantly increases with the size of the P(3-TSPM) lobe. Furthermore, the new method employed here can be universally applied to estimate the polarity of different types of particles.

Finally, the obtained JNP-Pickering emulsions, from styrene and methyl methacrylate, were polymerized in the presence of a hydrophobic radical initiator. Depending on the starting emulsion, o/w or w/o, we obtained either surface-nanostructured colloidosomes or polymeric hollow structures. Such hollow materials with closed cavities could be used as long-term storage containers for water-soluble actives such as proteins, enzymes, or pharmaceuticals.