SUPPORTING INFORMATION

Preparation of Organosoluble Silica-polypeptide Particles by “Click” Chemistry

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Weight loss profiles from TGA can be converted to the molar surface grafting density $\sigma$ using the general approach of Bartholome et al.\textsuperscript{51} We do not precisely follow their Eq. 1, though. The proposed expression is:

$$\sigma = \frac{f^{-1}w_{200-600} - w_{\text{silica}} \times [1 - f^{-1}w_{200-600}]}{M \times S_{\text{spec.}} \times [1 - f^{-1}w_{200-600}]} \times 10^6 \, (\mu\text{mol} \cdot m^{-2})$$  \hspace{1cm} (SI-1)

In the first term of the numerator, the measured fractional weight loss associated with decomposition of the polypeptide shell between 200 °C and 600 °C, defined as $w_{200-600}$, has been boosted by a factor $f^{-1}$ ($0 < f < 1$) representing the fraction of unattached PSLG polymer that decomposes between these two temperatures, measured separately. Thus, the term $f^{-1}w_{200-600}$ represents the fractional mass of shell material (or equivalently, the weight loss from a hypothetical 1 gram of the composite particle), assuming most material lost is polypeptide. Bartholome et al. did correct their weight loss for incomplete decomposition; we merely account for this effect explicitly by introducing the term $f^{-1}$. The purpose of the second term of the numerator is to subtract an estimate of the mass lost from the silica core; $w_{\text{silica}}$ is the fractional weight loss of silica between 200 °C and 600 °C, measured separately before grafting, and $[1 - f^{-1}w_{200-600}]$ is the mass of the silica core in a hypothetical 1 g sample of composite hybrid particles. It is assumed that this loss, mostly due to water and hydroxyl groups, takes place identically on the composite hybrid particles. In the denominator, the specific area of silica particles with radius 70 nm was computed using the density of silica, 1.98 g/mL, with the result $S_{\text{spec.}} = 22 \, \text{m}^2/\text{g}$; however, BET measurements suggest instead about $33 \, \text{m}^2/\text{g}$ for particles of similar size.\textsuperscript{52} The latter value is multiplied into
the core mass to obtain the core surface area. (Bartholome et al. omit the subtractive term, $- f^{-1} w_{200-600}$, when computing the core mass for their denominator; this will be unimportant for very thin shells, such as initiators.) The numerator is converted to a molar basis using the molecular weight of PSLG, $M_w = 8480$ g/mol. According to Figure 10 of the main article, $f \sim 0.95$, while $w_{\text{silica}} \sim 0.94 - 0.87 = 0.07$, while $w_{200-600} \sim 0.94 - 0.63 = 0.31$. This leads to $\sigma \sim 1.48 \mu\text{mol/m}^2$. The number of polymers per particle is $4\pi r_{\text{core}}^2 \sigma$. Using the core radius of 70 nm, this is about 55000 PSLG molecules/particle.

This number may be estimated using a slightly different approach. Noting that SiO$_2$ cores alone retain ~94% of their mass at 200°C, while hybrid particles retain ~62% of their mass (averaging the THF-produced and toluene-produced values) by 600°C, we imagine a 1-g sample of hybrid particle will contain 0.62 g at 600°C, but 5% ($f = 0.95$ as before) of this is polypeptide ash. Correcting for this gives 0.62 g of SiO$_2$. The polypeptide present would be 0.94 g (the mass after volatiles loss to 200°C) minus 0.62 g SiO$_2$, corrected for the $f = 0.95$ term, or $(0.94 - 0.62)/0.95 = 0.34$ g. The number of core particles can be obtained from the 0.62 g SiO$_2$ mass, assuming a spherical shape with $r = 70$ nm and a density of 1.98 g/cm$^3$. The number of PSLG molecules is computed from the 0.34 g and the polymer molar mass, leading to about 68,000 PSLG molecules per particle.

Still another estimate of the number of PSLG molecules per particle can be obtained from the DLS radii (70 nm for the core and 80 nm for the hybrid particle). The shell volume is $V_{\text{shell}} = \frac{4}{3} \pi (r_{\text{total}}^3 - r_{\text{core}}^3) = 7.08 \times 10^{-16}$ cm$^3$. Using the molecular weight
and density$^{33}$ of PSLG (~0.98 g/cm$^3$) one obtains 49100 molecules/particle. The average of the three methods is 57,000 PSLG molecules/particle (± 16%).

References

