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HIGH-DENSITY OLIGO(N-ISOPROPYLACRYLAMIDE) BRUSHES ON GOLD NANOPARTICLES UNDERGO PHASE TRANSITIONS

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In this study, we aim to investigate the thermo-responsive properties of the high-density oligomeric poly(N-isopropylacrylamide) (PNIPAM) brushes grafted onto monodisperse gold nano-core surfaces. First, we synthesized two batches of oligomeric PNIPAMs by RAFT polymerization. Second, to obtain the monodisperse fractions of PNIPAM oligomers, we fractionated one crude batch of molar mass ~ 900 g/mol. Third, we prepared gold nanoparticles using these PNIPAM oligomers as stabilizers, followed by fractionation of gold nanoparticles in order to achieve monodisperse particle samples which are of similar core sizes but stabilized with different oligomeric chain lengths. We then systematically characterized the particle samples with respect to the size of gold core, the PNIPAM coverage, and estimation of the surface grafting density.

To investigate the thermo-responsive properties of the oligomeric PNIPAM brushes, the gold nanoparticle dispersions in water were run in microcalorimetry, dynamic light scattering (DLS), and turbidity measurement, respectively. Calorimetric thermograms show a narrow and sharp dehydration transition peak centered at 30.0 °C for gold nanoparticles stabilized with PNIPAM 3300 g/mol, but a very broad peak centered at 10.5 °C for gold nanoparticles with oligomeric fraction 710 g/mol. DLS measurements performed at designed temperatures in the whole phase transition reveal that the former brush (i.e., the long chains) more behaves as linear PNIPAM freely dissolved in water, namely, forming a large aggregates after transition; while the latter one (i.e., the short chains) slightly aggregates. We explained the difference in property above in terms of the high surface density of oligomeric brushes and the structure which the brushes on the curved surface adopt.¹⁻²

References

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