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A series of all-acrylic poly(lauryl acrylate)−poly(benzyl acrylate) (PLA−PBzA) diblock copolymer nanoparticles are prepared by reversible addition−fragmentation chain transfer (RAFT) dispersion polymerization of benzyl acrylate in n-heptane, n-dodecane, or isohexadecane. As the PBzA block grows from the soluble PLA block it eventually becomes insoluble, which drives in situ polymerization-induced self-assembly (PISA). High monomer conversions (>99%) can be achieved and high blocking efficiencies are observed using 1H NMR spectroscopy and gel permeation chromatography, respectively. However, final *M*w/*M*n values range from 1.36 to 2.10, which suggests that chain transfer to polymer occurs in these all-acrylic PISA formulations. The soft, film-forming nature of these all-acrylic nanoparticles makes conventional TEM studies problematic. However, inspecting the visual appearance of these dispersions combined with DLS studies allows the construction of a phase diagram, which has been validated by cryo-TEM studies of selected copolymers. The latter technique confirms that spherical, worm-like or vesicular morphologies can be obtained depending on the copolymer concentration, mean degree of polymerization of the core and stabilizer blocks, and choice of solvent. Oscillatory rheology studies indicate that PLA−PBzA worms form free-standing worm gels at 20 °C with relatively low moduli (G′ ∼ 20 Pa). Moreover, reversible thermal transitions are observed below ∼15 °C and above ∼67 °C. Finally, worm gels that exhibit critical gelation concentrations as low as 2.5% w/w at 20 °C can be prepared at up to 40% w/w solids using a convenient one-pot protocol. In summary, this new PISA formulation represents a cost-effective, facile synthesis route to all-acrylic nano-objects in non-polar solvents.



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A poly(2-(dimethylamino)ethyl methacrylate) (PDMA) chain transfer agent was used for the reversible addition-fragmentation chain transfer alcoholic dispersion polymerisation of benzyl methacrylate (BzMA). THF GPC analysis indicated a well-controlled polymerisation and good blocking efficiency with no homopolymer contamination apparent. The PBzMA block becomes insoluble as it grows, leading to the *in situ* formation of sterically-stabilised diblock copolymer nanoparticles *via* polymerisation-induced self-assembly. Fixing the mean DP of the PDMA stabiliser block and varying the DP of the PBzMA block enabled a series of spherical nanoparticles of tuneable diameter to be obtained. These nanoparticles were characterised by TEM, DLS, MALLS and SAXS, with mean diameters ranging from 35 to 100 nm. The *N*agg values calculated from SAXS and MALLS are similar and scale approximately linearly with PBzMA DP. This suggests that spherical micelles grow in size not only as a result of the increase in copolymer molecular weight during the PISA synthesis, but also by exchange of individual copolymer chains between micelles and/or by sphere-sphere fusion events.

