

Branched poly(styrene-*b*-*tert*-butyl acrylate) and poly(styrene-*b*-acrylic acid) by ATRP from a dendritic poly(propylene imine)(NH₂)(64) core

With the aim of creating highly branched amphiphilic block copolymers, the primary amine end groups of the poly(propylene imine) dendrimers DAB-dendr(NH₂)(8) and DAB-dendr-(NH₂)(64) were converted to 2-bromoisobutyramide groups. Poly(styrene-*b*-*tert*-butyl methacrylate) (PS-*b*-PtBMA) was synthesized by ATRP from the eight end group initiator, and polystyrene-*b*-*tert*-butyl acrylate) (PS-*b*-PtBA) was synthesized from the 64 end group initiator. The *tert*-butyl groups were removed to produce polystyrene-*b*-methacrylic acid) (PS-*b*-PMAA) and polystyrene-*b*-acrylic acid) (PS-*b*-PAA).

Comparison of size exclusion chromatography (SEC) absolute molecular weight analyses of the polystyrenes with calculated molecular weights showed that the eight end group initiator produced a polystyrene with about eight branches, and that the 64 end group initiator produced polystyrene with many fewer than 64 branches. The PS-*b*-PtBA materials also have many fewer than 64 branches. The PS-*b*-PAA samples dissolved molecularly in DMF but formed aggregates in water even at pH 10. AFM images of the PS-*b*-PtBAs spin coated from THF and DMF onto mica showed aggregates. AFM images of the PS-*b*-PAAs spin coated from various mixtures of DMF and water at pH 10 showed flat disks and worm-like images similar to those observed with linear PS-*b*-PAAs. Use of a PS-*b*-FAA and a PS-*b*-PMAA as templates for emulsion polymerization of styrene produced latexes 100-200 nm in diameter.

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