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Novel Synthesis of Surface-Grafted Radical Initiator With Improved Stability and Yield ERICH BAIN, KEITH DAWES, Department of Chemical and Biomolecular Engineering, North Carolina State University, XIN-FANG HU, CHRISTOPHER GORMAN, Department of Chemistry, North Carolina State University, JIRI SROGL, Institute of Chemistry & Biochemistry, Academy of Sciences of the Czech Republic, JAN GENZER, Department of Chemical and Biomolecular Engineering, North Carolina State University — Polymers grafted at interfaces are attractive for applications including antifouling coatings, biologically functionalized materials, and responsive surfaces. The "grafting from" approach to form densely packed brushes involves functionalizing a substrate with initiating moieties, and carrying out polymerization, e.g., surface-initiated free-radical polymerization (SI-FRP). Azo initiators for SI-FRP are commonly synthesized by a low-yielding route requiring large amounts of potassium cyanide. Those initiators are linked to a substrate by means of an ester group, rendering tethered polymers susceptible to degrafting by hydrolysis. We present a novel synthetic route to an asymmetric azo initiator, whose yield is nearly double that of previous syntheses. Cyanide usage in the new method is reduced by 72 percent. The spacer linking the initiator to a substrate contains only carbon-carbon bonds, resulting in stable brushes. Results are demonstrated for SI-FRP as well as reverse ATRP and RAFT.

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