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Synthesis and characterisation of anionic pentablock brush copolymers bearing poly(acrylic acid) side chains on the brush blocks separated by linear poly(butyl methacrylate) blocks

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## ACCEPTED MANUSCRIPT

### SYNTHESIS AND CHARACTERISATION OF ANIONIC PENTABLOCK BRUSH COPOLYMERS BEARING POLY(ACRYLIC ACID) SIDE CHAINS ON THE BRUSH BLOCKS SEPARATED BY LINEAR POLY(BUTYL METHACRYLATE) BLOCKS

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#### ABSTRACT

One-pot successive three-step RAFT polymerization of 2-hydroxyethyl methacrylate (HEMA) and butyl methacrylate (BMA) in the presence of difunctional RAFT CTA is reported demonstrating successful synthesis of pentablock copolymers containing hydrophilic blocks of pHEMA separated by hydrophobic blocks of pBMA. Dispersity of pentablock copolymers was lower than that of pHEMA and triblock copolymers, down to 1.11. pHEMA blocks of the pentablock copolymer were decorated by pendent butylthiocarbonothioylthio moieties, which served as multiple RAFT CTA for grafting of acrylic acid (AA). The resulting anionic pentablock brush copolymers consisting of three brush blocks separated by linear blocks were characterized by SEC with triple detection and <sup>1</sup>H NMR spectroscopy. Pentablock brush copolymers with short pAA side chains produced aggregates at low pH and showed conformational changes during titration with alkaline solution, while those with medium-length pAA side chains showed ionization behaviour typical for anionic molecular brushes. Anionic pentablock brush copolymers are mimicking naturally occurring molecular brushes and deserve attention as potential surface modifiers and lubricants.

**KEYWORDS:** RAFT polymerization, pentablock copolymers, brush copolymers, anionic molecular brushes, one-pot synthesis.

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