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Preparation of dual stimuli-responsive block copolymers based on different activated esters with distinct reactivities

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Abstract: In the present study, we described a facile method for introducing functional moieties into block copolymer structures by sequential aminolysis of pentafluorophenyl acrylate (PFPA) ester and methyl salicylate acrylate (MSA) ester. For the first time, reversible addition-fragmentation transfer (RAFT) polymerization of MSA yielding block copolymers poly(MSA)-*b*-poly(PFPA) was reported. The yielded block copolymers were subsequently modified step-by-step using amino moieties, affording polymers with bespoke functionality. By exploring the reactivity difference of two activated esters (PFPA and MSA) toward amines, the installation of amine functionalities on polymer backbones while maintaining a block copolymer architecture was realized in a controlled manner. The selective reactivity of these two esters (PFPA and MSA) towards aliphatic amines, such as isopropylamine, cyclopropylamine and *N,N*-diethylethylenediamine, provided a novel synthetic approach in making temperature and pH dual responsive polymers. Finally, the self-assembly behavior of the obtained block copolymers was investigated.

Keywords: methyl salicylate acrylate ester; pentafluorophenyl acrylate ester; post-polymerization modification; RAFT polymerization; stimuli responsive polymers; block copolymers

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