

Electronic Supplementary Information (ESI)

**Consecutive living polymerization from cationic to radical:
A straightforward yet versatile methodology for the precision
synthesis of “cleavable” block copolymers with a hemiacetal
ester junction**

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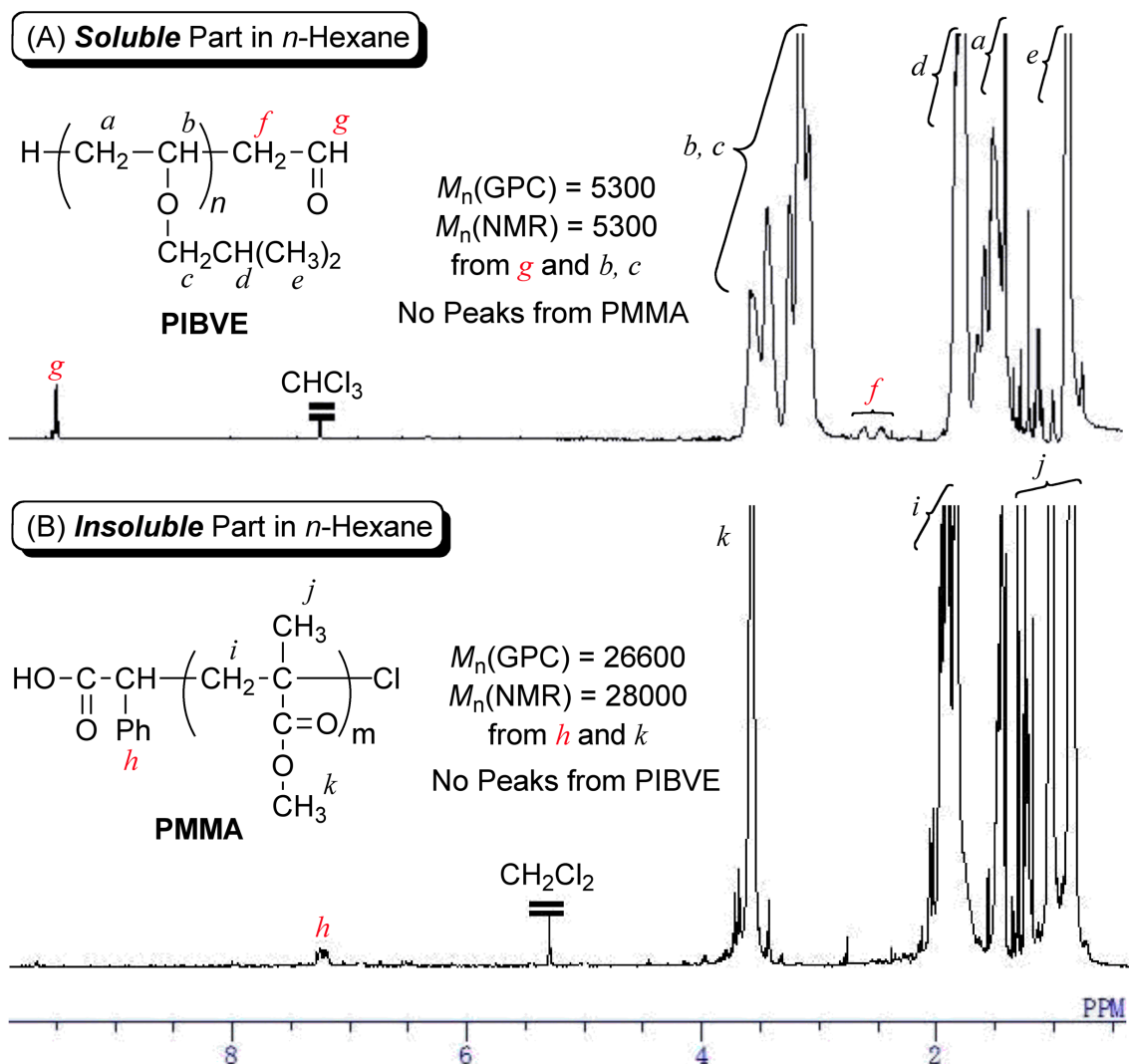


Figure S1. Structure analyses by ¹H NMR (500 MHz, CDCl₃, r.t.) after fractional precipitation with *n*-hexane in a TFA-cleavage experiment on PIBVE-*b*-PMMA carrying an HAE junction: (A) soluble part in *n*-hexane, (B) insoluble part in *n*-hexane.

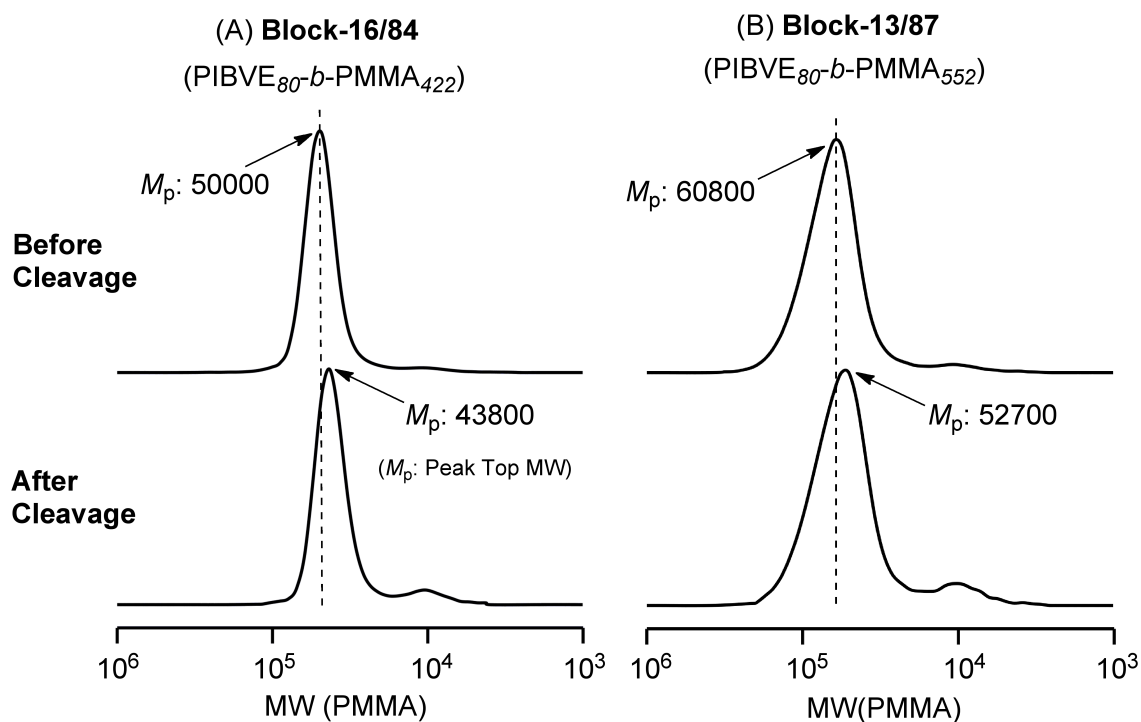


Figure S2. SEC analyses for a piece of cast films with HAE-connected PIBVE-*b*-PMMA [Block-16/84 (A) and -13/87 (B)] in cleavage experiments (upperpart: before the cleavage, downpart: after the cleavage). Cleavage treatment: immersion of the cast films in 0.1 vol% TFA solution of *n*-hexane.

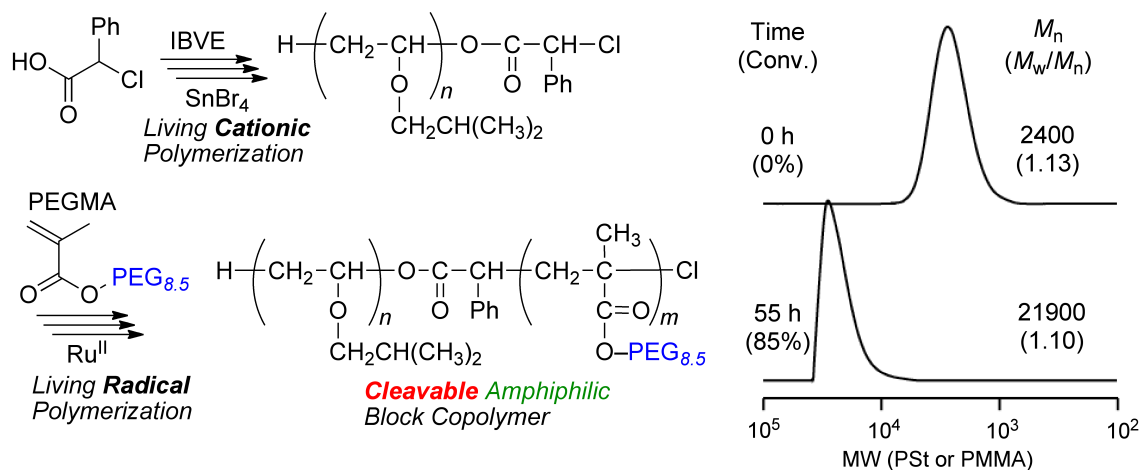


Figure S3. Ruthenium-catalyzed living radical polymerization of PEGMA with PIBVE macro initiator in toluene at 80°C: [PEGMA]₀ = 500 mM, [PIBVE]₀ = 5.0 mM, [RuCl(Ind)(PPh₃)₂]₀ = 0.5 mM, [*n*-Bu₃N]₀ = 5.0 mM. The PIBVE macroinitiator was prepared via living cationic polymerization of IBVE with CPAA as an initiator in conjunction with SnBr₄ catalyst.