Ultrahigh Molecular Weight Linear Block Copolymers: Rapid Access by Reversible-Deactivation Radical Polymerization and Self-Assembly into Large Domain Nanostructures

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Synthesis and NMR characterization of PSM-PS block copolymers

SK-1: Poly(SM) ($M_n = 512,600$ g/mol, 1.092 g, 2.07 μmol) and AIBN (30 μL of 7 mM stock solution, 0.21 μmol) were dissolved in (17.2 mL, 165.3 mmol) of styrene in a reaction flask equipped with a stir bar. This mixture was allowed to stir until the solids were completely dissolved. The mixture was then bubbled with N₂ for 15 minutes, and placed in an oil bath at 65 °C. After 24 h, the flask was cooled to room temperature and the contents were diluted with dichloromethane and precipitated in hexanes (twice). The resulting polymer was suspended in boiling acetonitrile to remove residual poly(SM) homopolymer. The polymer was then dried overnight under vacuum to yield a powdery solid (0.918 g). SEC (polystyrene calibration): $M_n = 176$ kg/mol, $D = 1.49$; $^1$H NMR: $n$(PS) = 4,362.
**SK-2** : Poly(SM) \( (M_n = 401,900 \text{ g/mol}, 0.096 \text{ g}, 0.24 \mu\text{mol}) \) and AIBN \( (3.4 \mu\text{L of 7 mM stock solution, 0.02 \mu\text{mol}}) \) were dissolved in \( (1.1 \text{ mL, 9.25 mmol}) \) of styrene in a reaction flask equipped with a stir bar. This mixture was allowed to stir until the solids were completely dissolved. The mixture was then bubbled with \( \text{N}_2 \) for 15 minutes, and placed in an oil bath at 65 °C. After 24 h, the flask was cooled to room temperature and the contents were diluted with dichloromethane and precipitated in hexanes (twice). The resulting polymer was suspended in boiling acetonitrile to remove residual poly(SM) homopolymer. The polymer was then dried overnight under vacuum to yield a powdery solid (0.094 g). SEC (polystyrene calibration): \( M_n = 296 \text{ kg/mol}, D = 1.63; ^1\text{H NMR: } n(\text{PS}) = 2,880. \)
**SK-3:** Poly(SM) ($M_n = 512,600$ g/mol, 0.991 g, 1.88 $\mu$mol) and AIBN (20 $\mu$L of 7 mM stock solution, 0.14 $\mu$mol) were dissolved in (31.2 mL, 271.8 mmol) of styrene in a reaction flask equipped with a stir bar. This mixture was allowed to stir until the solids were completely dissolved. The mixture was then bubbled with N\(_2\) for 15 minutes, and placed in an oil bath at 65 °C. After 24 h, the flask was cooled to room temperature and the contents were diluted with dichloromethane and precipitated in hexanes (twice). The resulting polymer was suspended in boiling acetonitrile to remove residual poly(SM) homopolymer. The polymer was then dried overnight under vacuum to yield a powdery solid (1.02 g). SEC (polystyrene calibration): $M_n = 213$ kg/mol, $D = 1.39$; $^1$H NMR: $n$(PS) = 8,341.
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**SK-4**: Poly(SM) ($M_n = 431,900$ g/mol, 0.621 g, 1.48 μmol) and AIBN (20 μL of 7 mM stock solution, 0.14 μmol) were dissolved in (12.5 mL, 108.5 mmol) of styrene in a reaction flask equipped with a stir bar. This mixture was allowed to stir until the solids were completely dissolved. The mixture was then bubbled with N2 for 15 minutes, and placed in an oil bath at 65 °C. After 24 h, the flask was cooled to room temperature and the contents were diluted with dichloromethane and precipitated in hexanes (twice). The resulting polymer was suspended in boiling acetonitrile to remove residual poly(SM) homopolymer. The polymer was then dried overnight under vacuum to yield a powdery solid (1.116 g). SEC (polystyrene calibration): $M_n = 427$ kg/mol, $D = 1.64$; $^1$H NMR: $n(PS) = 6,554$. 

![SK-4](image-url)
SK-5: Poly(SM) ($M_n = 401,900$ g/mol, 0.056 g, 0.14 μmol) and AIBN (1.9 μL of 7 mM stock solution, 0.013 μmol) were dissolved in (1.4 mL, 11.9 mmol) of styrene in a reaction flask equipped with a stir bar. This mixture was allowed to stir until the solids were completely dissolved. The mixture was then bubbled with N₂ for 15 minutes, and placed in an oil bath at 65 °C. After 24 h, the flask was cooled to room temperature and the contents were diluted with dichloromethane and precipitated in hexanes (twice). The resulting polymer was suspended in boiling acetonitrile to remove residual poly(SM) homopolymer. The polymer was then dried overnight under vacuum to yield a powdery solid (0.085 g). SEC (polystyrene calibration): $M_n = 339$ kg/mol, $Đ = 1.76$; $^1$H NMR: $n(PS) = 5,419$. 

![SK-5](image_url)
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**SK-6**: Poly(SM) \( (M_n = 431,900 \text{ g/mol}, 0.621 \text{ g}, 1.48 \mu\text{mol}) \) and AIBN \((20 \mu\text{L of 7 mM stock solution, 0.14 \mu\text{mol})}\) were dissolved in \((12.5 \text{ mL, 108.5 mmol})\) of styrene in a reaction flask equipped with a stir bar. This mixture was allowed to stir until the solids were completely dissolved. The mixture was then bubbled with \(\text{N}_2\) for 15 minutes, and placed in an oil bath at 65 °C. After 24 h, the flask was cooled to room temperature and the contents were diluted with dichloromethane and precipitated in hexanes (twice). The resulting polymer was suspended in boiling acetonitrile to remove residual poly(SM) homopolymer. The polymer was then dried overnight under vacuum to yield a powdery solid \((0.806 \text{ g})\). SEC (polystyrene calibration): \(M_n = 218 \text{ kg/mol}, D = 1.56\); \(^1\text{H NMR: } n(\text{PS}) = 11,234\).
**Supporting Information**

**Figure S1.** Polymerization of MMA ([MMA]:[CDB]:[Me₆TREN] = 2,000:1:1). (A) Synthetic scheme, (B) SEC analysis of PMMA homopolymers, (C) first-order kinetic plot, and (D) evolution of molecular weight and dispersity with conversion.

**Figure S2.** Polymerization of HEMA ([HEMA]:[CDB]:[Me₆TREN] = 2,000:1:1). (A) Synthetic scheme, (B) SEC analysis of Acetylated PHEMA homopolymers, (C) first-order kinetic plot, and (D) evolution of molecular weight and dispersity with conversion.
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Figure S3. SEC traces of (a) PSM precursor, and PSM-PS block copolymer SK-3: (b) as synthesized, (c) after washing in boiling acetonitrile, and (d) after washing in cyclohexane.

Figure S4. Differential scanning calorimetry analysis of PSM-PS block copolymer.
Figure S5. USAXS and SEM analysis of PSM-PS block copolymers (A) SK-5, and (B) SK-6.