Supporting information

Synthesis of Chain End Acyl-Functionalized Polymers by Living Anionic Polymerization: Versatile Precursor for H-Shaped Polymers

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Synthesis of chain end acyl-functionalized PIsp.

A difunctional living PIsp was obtained by the anionic polymerization of Isp (0.43 g, 6.25 mmol) with K-Naph (0.147 mmol) in THF at −78 °C for 4 h (Table 1, run 9). DPE (0.265 mmol, 1.6 equivalent) in THF (2 mL) was added at −78 °C and reacted for 15 min. A THF solution (6 mL) of 1 (0.286 mmol, 1.9 equivalent) was then added at −78 °C to the solution of DPE-capped living PIsp and reacted for 2 h. Finally, the end-functionalization was terminated with degassed AcOH. A white polymer (0.51 g, 96%) was obtained by pouring reaction solution into MeOH. The resulting PIsp was purified by reprecipitation in MeOH and freeze-drying from the benzene solution.

$^1$H NMR (400 MHz; CDCl$_3$; ppm) $\delta = 1.20-2.35$ (br, main chain), 1.72 (br, 24H, adamantyl), 1.95-2.03 (br, 36H, adamantyl), 3.74 (s, 2H, terminal CH), 4.69-5.74 (br, olefin protons, 7.05-7.41 (br, aromatic).

$^{13}$C NMR (100 MHz; CDCl$_3$; ppm): $\delta = 16.5-42.4$ (-CH$_3$), 28.3 (adamantyl), 36.7 (adamantyl), 40.2 (adamantyl), 36.7-50.0 (main chain), 47.0 (adamantyl), 110.6-111.6 (=CH$_2$), 126.0-128.3 (Ar), 136-139 (-CH=CH$_2$), 147.2-148.9 (-C(CH$_3$)=CH$_2$), 209.1 (C=O).

IR (KBr; cm$^{-1}$): 3072, 2923, 2362, 1780, 1668 (C=O), 1644 (=CH$_2$), 1602, 1448, 1411, 1374, 885, 699.
Synthesis of H-shaped block copolymer of St and 2VP.

A living P2VP anion was firstly prepared by the polymerization of 2VP (0.98 g, 9.31 mmol) with sec-BuLi (0.0892 mmol) and DPE (0.161 mmol) in THF at –78 °C. Then, to the solution of the P2VP anion, a THF solution of chain end acyl tetra-functionalized PSt \( (M_n = 3.9 \text{ kg/mol}, 0.0181 \text{ mmol}) \) was added at –78 °C and reacted for 24 h. During the reaction, the red coloration of the living P2VP was maintained. Finally, the reaction was terminated with MeOH. A polymer of white powder was obtained by pouring reaction solution to hexane. A bimodal GPC curve of the reaction system was obtained, which was corresponding to the objective H-shaped block copolymer and the excess amount of P2VP branch. The H-shaped block copolymer was isolated in 39% yield by repeating fractional precipitations (ethanol/hexane), and purified by freeze-drying from the benzene solution.

\(^{1}\)H NMR (400 MHz; CDCl\(_3\); ppm) \( \delta = 0.58-0.72 \) (m, 24H, \( \text{CH}_3\text{CH}_2\text{CHC}_3 \)), \( 0.98-2.41 \) (br, backbone and adamantyl), \( 3.75 \) (s, 2H, terminal CH), \( 6.15-7.25 \) (br, Ar), \( 8.06-8.43 \) (br, 6-position in pyridine ring).

IR (KBr; cm\(^{-1}\)) 3004, 2930, 1590, 1567, 1473, 1433, 1148, 747, 700.
Figure S1. $^1$H NMR spectrum of run 2.

Figure S2. $^{13}$C NMR spectrum of run 2.
Figure S3. FT-IR spectra of 1 (A) and run 2 (B).

Figure S4. $^1$H NMR spectrum of run 8.
Figure S5. $^{13}$C NMR spectrum of run 8.

Figure S6. $^1$H NMR spectrum of run 9.
**Figure S7.** $^{13}$C NMR spectrum of run 9.

**Figure S8.** MALDI-TOF-MS spectrum of run 9.
**Figure S9.** $^1$H NMR spectrum of run 10.

**Figure S10.** $^{13}$C NMR spectrum of run 10.
**Figure S11.** MALDI-TOF-MS spectrum of run 10.

**Figure S12.** $^1$H NMR spectrum of H-shaped PSt.
**Figure S13.** IR spectra of starting acyl end-functionalized telechelic PST (A), and H-shaped PST (B).

**Figure S14.** GPC curves of starting acyl end-functionalized telechelic PST (A), the crude product after the grafting reaction (B), and the isolated H-shaped block copolymer with St and 2VP (C).
Figure S15. $^1$H NMR spectrum of H-shaped copolymer with St and 2VP.

Figure S16. IR spectra of starting acyl end-functionalized telechelic PSt (A), and H-shaped copolymer with St and 2VP (B).
Figure S17. $^1$H NMR spectrum of 1-adamantanyl 4-bromophenyl ketone.

Figure S18. $^{13}$C NMR spectrum of 1-adamantanyl 4-bromophenyl ketone.
Figure S19. $^1$H NMR spectrum of 2-(1-adamantyl)-2-(4-bromophenyl)-1,3-dioxolane.

Figure S20. $^{13}$C NMR spectrum of 2-(1-adamantyl)-2-(4-bromophenyl)-1,3-dioxolane.
Figure S21. $^1$H NMR spectrum of 1.

Figure S22. $^{13}$C NMR spectrum of 1.