Supplementary Information for:

Synthesis of Mixed Poly(ε-caprolactone)/Polystyrene Brushes from Y-Initiator-Functionalized Silica Particles by Surface-Initiated Ring-Opening Polymerization and Nitroxide-Mediated Radical Polymerization

Weikun Li,[†] Chunhui Bao,[†] Roger A. E. Wright, and Bin Zhao*

Department of Chemistry, University of Tennessee, Knoxville, TN 37996, United States

[†]Contributed equally to the work. * Corresponding author. Email: <u>zhao@ion.chem.utk.edu</u>



Figure S1. Thermogravimetric analysis (TGA) of (a) Y-initiator-functionalized silica particles (YI-P-1), (b) PCL brush-grafted silica particles with PCL $M_{n,SEC}$ of 25.8 kDa synthesized from YI-P-1, and (c) mixed PCL/PS brush-grafted silica particles with PCL $M_{n,SEC}$ of 25.8 kDa and PS $M_{n,SEC}$ of 24.5 kDa. TGA was performed in air at a heating rate of 20 °C/min from room temperature to 800 °C.



Figure S2. Thermogravimetric analysis (TGA) of (a) Y-initiator-functionalized silica particles (YI-P-2), (b) PCL brush-grafted silica particles with PCL $M_{n,SEC}$ of 25.4 kDa synthesized from YI-P-2, and (c) mixed PCL/PS brush-grafted silica particles with PCL $M_{n,SEC}$ of 25.4 kDa and PS $M_{n,SEC}$ of 25.2 kDa. TGA was performed in air at a heating rate of 20 °C/min.



Figure S3. Thermogravimetric analysis (TGA) of (a) Y-initiator-functionalized silica particles (YI-P-4), (b) PCL brush-grafted silica particles with PCL $M_{n,SEC}$ of 24.0 kDa synthesized from YI-P-4, and (c) mixed PCL/PS brush-grafted silica particles with PCL $M_{n,SEC}$ of 24.0 kDa and PS $M_{n,SEC}$ of 24.0 kDa. TGA was performed in air at a heating rate of 20 °C/min from room temperature to 800 °C.



Figure S4. Thermogravimetric analysis (TGA) of (a) Y-initiator-functionalized silica particles (**YI-P-5**), (b) PCL brush-grafted silica particles with PCL $M_{n,SEC}$ of 25.6 kDa synthesized from **YI-P-5**, and (c) mixed PCL/PS brush-grafted silica particles with PCL $M_{n,SEC}$ of 25.6 kDa and PS $M_{n,SEC}$ of 24.3 kDa. TGA was performed in air at a heating rate of 20 °C/min from room temperature to 800 °C.



Figure S5. Thermogravimetric analysis (TGA) of (a) Y-initiator-functionalized silica particles (**YI-P-6**), (b) PCL brush-grafted silica particles with PCL $M_{n,SEC}$ of 27.1 kDa synthesized from **YI-P-6**, and (c) mixed PCL/PS brush-grafted silica particles with PCL $M_{n,SEC}$ of 27.1 kDa and PS $M_{n,SEC}$ of 24.2 kDa. TGA was performed in air at a heating rate of 20 °C/min from room temperature to 800 °C.



Figure S6. Thermogravimetric analysis (TGA) of (a) Y-initiator-functionalized silica particles (**YI-P-7**), (b) PCL brush-grafted silica particles with PCL $M_{n,SEC}$ of 24.2 kDa synthesized from **YI-P-7**, and (c) mixed PCL/PS brush-grafted silica particles with PCL $M_{n,SEC}$ of 24.2 kDa and PS $M_{n,SEC}$ of 23.8 kDa. TGA was performed in air at a heating rate of 20 °C/min from room temperature to 800 °C.