

Langmuir-Schaefer (LS) Macroinitiator Film Control on the Grafting of a Thermosensitive Polymer Brush via Surface Initiated-ATRP

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**RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required
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Experimental

Esterification of 2-hydroxyethyl methacrylate (HEMA) with 2-bromoisobutyrylbromide (2-BiBB), HeBiB. In a 250-mL three neck flask, 9.48 mL (68.388 mmol) of triethylamine (TEA) and 8.90 g (68.388 mmol) of HEMA were added and dissolved in 15 mL of dry THF. The reaction mixture was stirred at RT for 5 min and then in an ice bath at 0°C. 19.65 g (85.485 mmol) of 2-BiBB was added dropwise to the cooled solution for a period of 1 h under a N₂ atmosphere. After the addition was completed, the reaction mixture was allowed to react at 0°C for 5 min and then was left stirring at RT for an additional 12 h. Excess solvent was evaporated and the crude product was redissolved in CH₂Cl₂. Purification was done by extraction and flash column chromatography. (79.5% product yield) The purified oily product was dried under vacuum and stored in a refrigerator until further use. ¹H NMR (300 MHz, CDCl₃) δ(ppm): 6.12 (d, 1H), 5.64 (d, 1H), 4.46 (m, 4H), 1.95 (s, 9H).

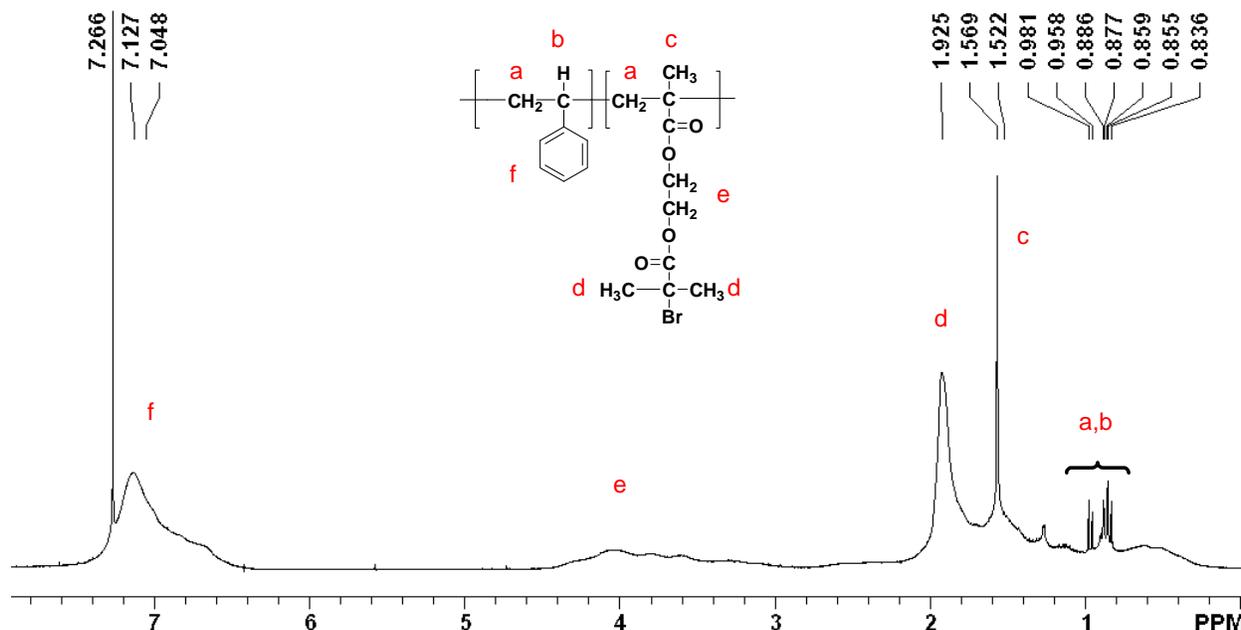


Figure S1. ¹H NMR recorded in CDCl₃ of the amphiphilic macroinitiator p(St-co-HeBiB) using a 3:1 molar ratio of styrene to HeBiB. The polymer was precipitated in excess hexane.

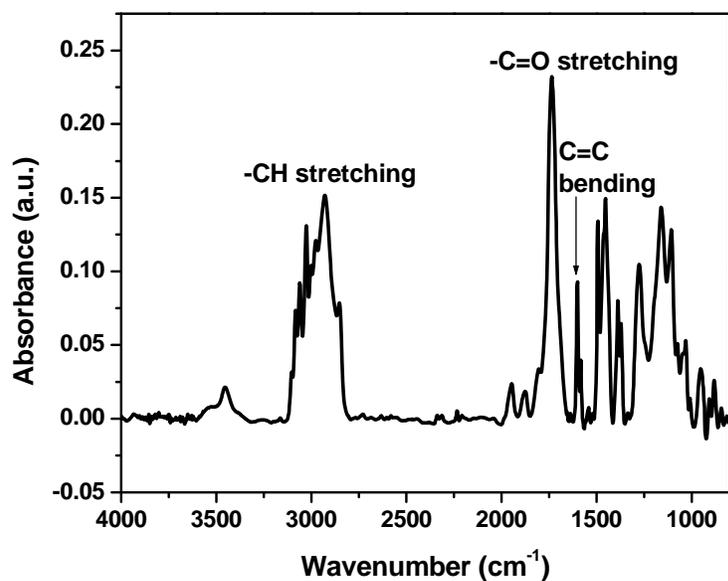


Figure S2. FT-IR spectrum of p(St-co-HeBiB) macroinitiator powder using a KBr pellet.

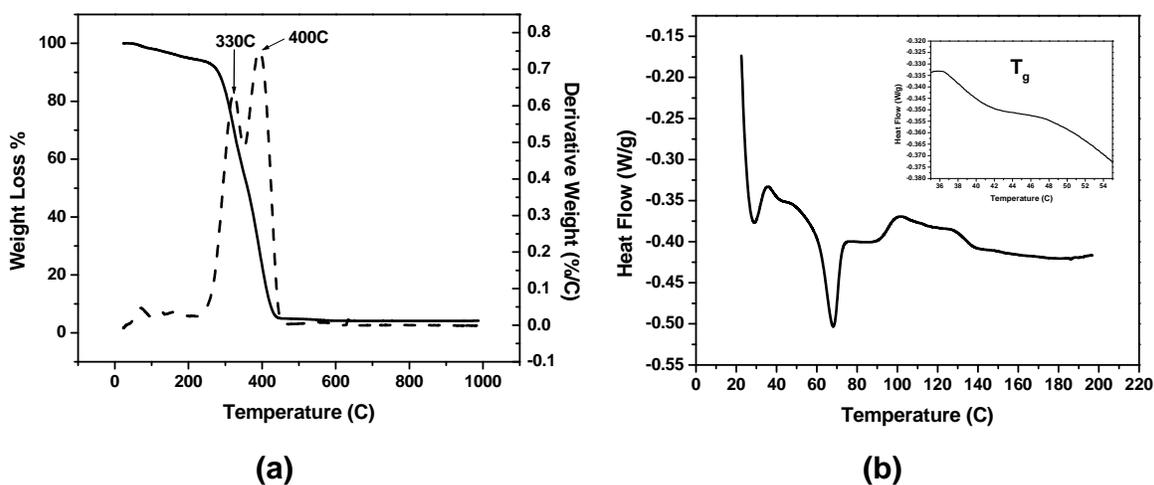


Figure S3. TGA (a) and DSC (b) thermograms of p(St-co-HeBiB) macroinitiator. The inset in (b) shows the T_g of the macroinitiator.

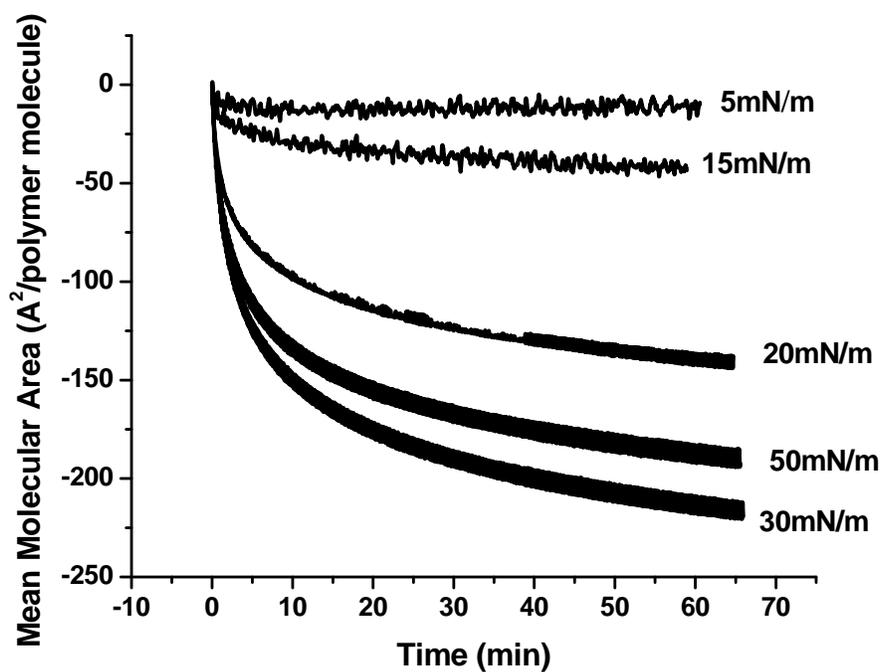
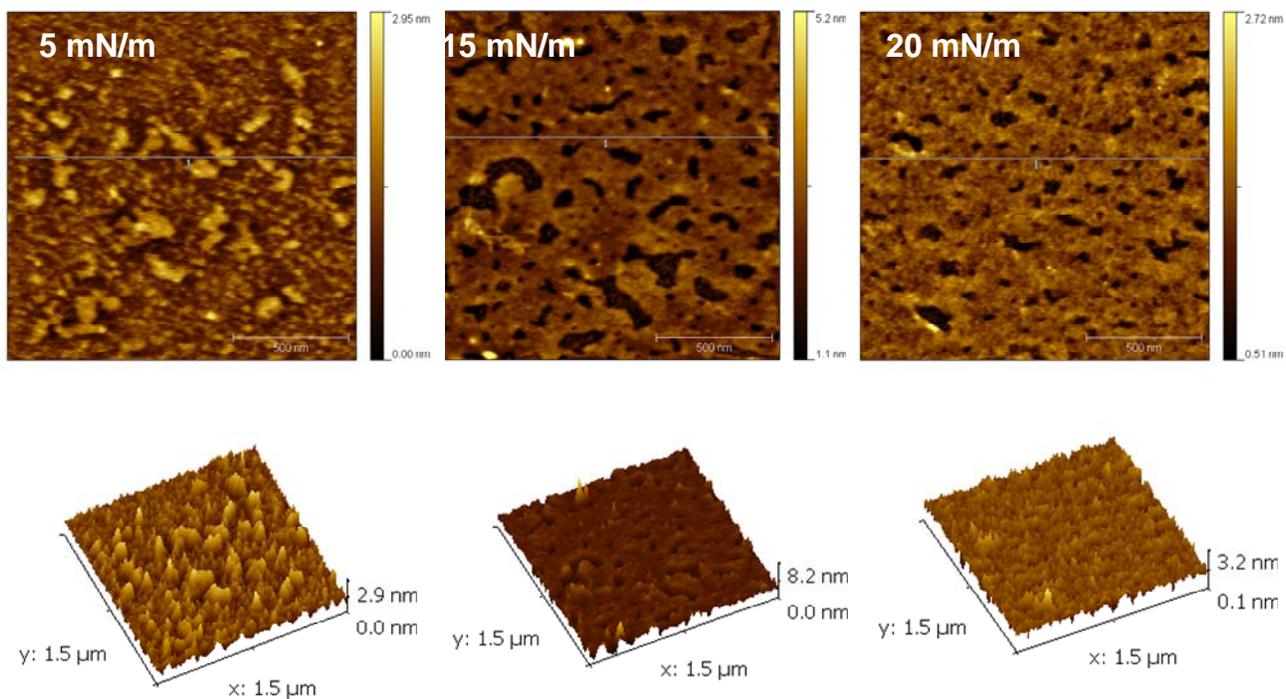


Figure S4. Time dependence of A when π was kept constant.



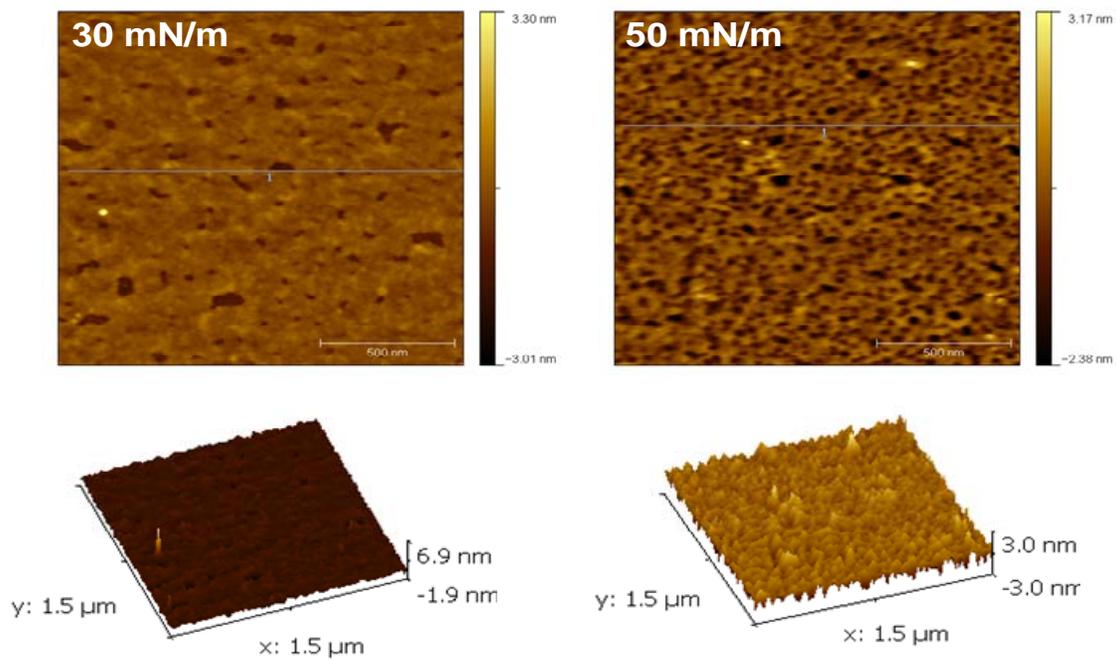


Figure S5. AFM and 3D images of the LS macroinitiator films.

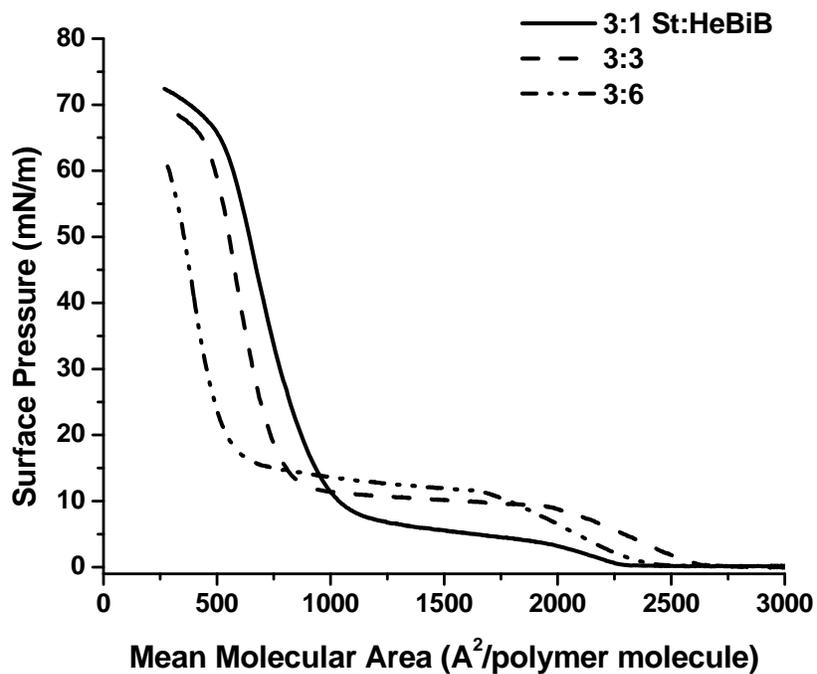


Figure S6. π -A isotherm of p(St-co-HeBiB) macroinitiator with different monomer ratios.