

### Supporting Information

**Materials.** All thiophene derivatives, triethyl amine (TEA), 2-bromoisobutyrylbromide, copper bromide (CuBr), iron chloride (FeCl<sub>3</sub>), pentamethyldiethylenetriamine (PMDETA) were used as received without further purification. *n*-butyl or *t*-butyl acrylate monomers (noted *n*BuA or *t*BuA respectively) were dried and distilled over CaH<sub>2</sub>. THF was dried and distilled over CaH<sub>2</sub> and sodium/benzophenone respectively. CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> were dried and distilled over CaH<sub>2</sub>. All reactions were carried out under a dry nitrogen atmosphere, using flame-dried glassware.

**Synthesis of 2-thiophene ATRP initiator 1 (or 1').** To a three-neck flask, 1.5 eq of triethylamine (TEA) were added to a THF (50 ml) solution of 2-thiophene methanol (or ethanol) (1.992 g, 1eq). After cooling down, a THF (10 ml) solution of 2-bromoisobutyrylbromide was added drop-wise to the reaction mixture. Once the addition was completed, the reaction was let to room temperature and stirred for 24h. Then, the reaction mixture was filtered in order to remove the ammonium salts and concentrated. The product was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and washed three times with water, subsequently dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residual product was purified by passing through a silica gel column using CH<sub>2</sub>Cl<sub>2</sub> as the eluant. The appropriate fractions were collected and the solvent was removed to give 3.532 g of the pure product 1 (or 1') (82 % yield).

**Synthesis of PHT-*b*-PtBuA copolymers. (Route 1).** (i) To a round-bottom flask containing the mixture of initiator 1 (1 eq), CuBr (1 eq) and PMDETA (1 eq), the appropriate amount of *t*BuA monomer was added (targeted  $\overline{M}_n=5000$  g/mol.). The reaction mixture was degassed by means of three freeze-thaw cycles and kept under stirring during 16 min at 80°C. After, the copper was removed by filtration on neutral alumina column. At the end, the  $\alpha$ -(2-

thienyl)-PtBuA (**2**) was precipitated in a cold MeOH/H<sub>2</sub>O (70/30) (v/v) mixture and dried under vacuum at room temperature. **(ii)** In a three-neck flask equipped with a condenser, FeCl<sub>3</sub> ( $r = [\text{FeCl}_3]/[\text{hexylthiophene}] =$  from 3 to 4) was added in CH<sub>2</sub>Cl<sub>2</sub>. A CH<sub>2</sub>Cl<sub>2</sub> (about 50 ml of solvent for 0.15 g of FeCl<sub>3</sub>) solution of  $\alpha$ -(2-thienyl)-PtBuA (1eq) and 3-hexylthiophene (from 2 to 20 eq) was then added drop-wise. After 24h of stirring under nitrogen, the reaction was stopped by addition of NH<sub>4</sub>OH aq. The aqueous layer was washed with CH<sub>2</sub>Cl<sub>2</sub> and leftover. The CH<sub>2</sub>Cl<sub>2</sub> organic extracts were washed with distilled water and dried over Na<sub>2</sub>SO<sub>4</sub>. The organic fraction was concentrated by rotary evaporation and the final copolymer PHT-*b*-PtBuA was precipitated at low temperature in pentane.

**Synthesis of PnBuA-*b*-PHT-*b*-PnBuA triblock copolymers. (Route 2).** **(i)** To a three-neck flask equipped with a condenser were added 6,18 g ( $38.10^{-3}$  mol.) of FeCl<sub>3</sub> and CHCl<sub>3</sub> (180 ml). Then a solution (125 ml) of 1.71 g ( $6.18.10^{-3}$  mol.) of **1'** and 0.8 g ( $4.75.10^{-3}$  mol.) of 3-hexylthiophene in CHCl<sub>3</sub> was added drop-wise. After 24h of stirring under nitrogen, the reaction was stopped by addition of NH<sub>4</sub>OH aq. The same purification procedure as above was followed. Pure product **3** was obtained in 10 % yield. **(ii)** In a second step, 0.4543 g ( $3.73.10^{-3}$  mol.) of the  $\alpha,\omega$ -dibromo-functionalized PHT (**3**) obtained was introduced in a round-bottom flask with the same proportion of the CuBr/PMDETA complex as the precedent route. Then 0.74 g ( $5.82.10^{-3}$  mol.) of *n*BuA was added. The reaction mixture was degassed and kept under stirring during 1h30 at 50°C. Following the usual purification procedure after ATRP (see above), the PnBuA-*b*-PHT-*b*-PnBuA triblock copolymer was obtained (97 % yield).

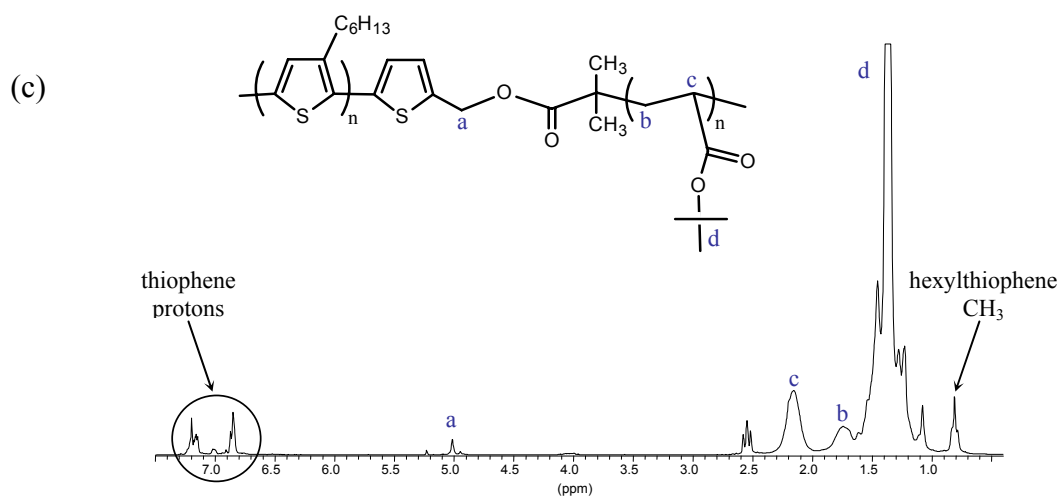
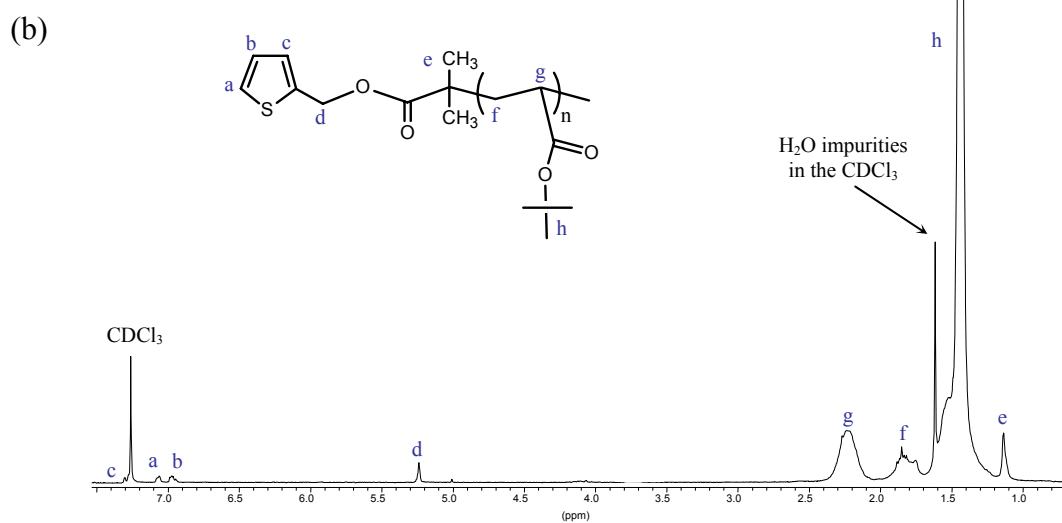
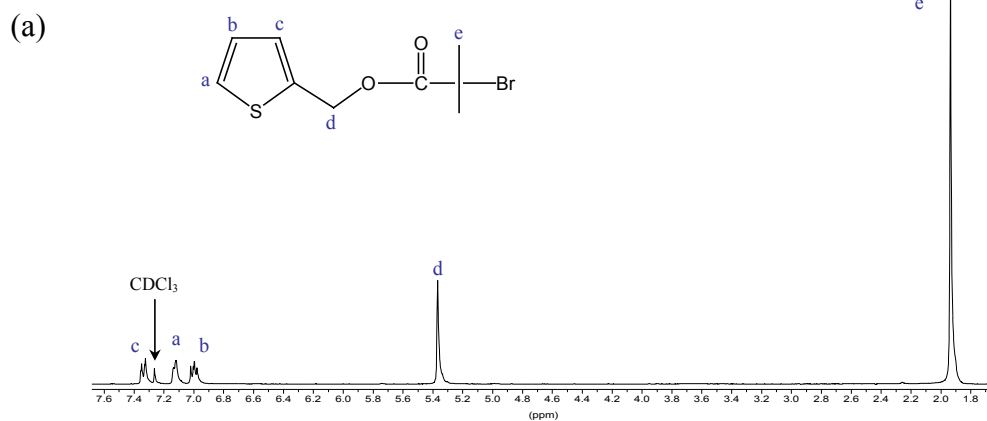
**Analytical techniques.** The purity of each product and polymer was determined by means of size exclusion chromatography (SEC) in THF calibrated with polystyrene standards and <sup>1</sup>H

NMR (Bruker AC400© spectrometer) in CD<sub>2</sub>Cl<sub>2</sub> or CDCl<sub>3</sub>. Static light scattering (SLS) and dynamic light scattering (DLS) measurements were performed on a ALV5000 goniometer equipped with a ALV5000/E Multiple Tau Digital Realtime correlator (see more details in a following paragraph). The cyclic voltammetry measurements were performed with a Tacussel apparatus (PGSTAT10). The analysis of the sample solutions were carried out in CH<sub>2</sub>Cl<sub>2</sub> (HPLC grade, Fisher Scientific) containing 0.1 M of tetrabutylammonium hexafluorophosphate (TBA<sup>+</sup>PF<sub>6</sub><sup>-</sup>) as supporting electrolyte in a one-compartment cell equipped with three electrodes. The working anode was platinum, the counter-electrode a platinum wire and the reference electrode being a saturated calomel electrode (SCE). UV-vis spectra were carried out in cyclohexane solutions, and recorded on a Varian Cary 3E UV-visible Spectrophotometer. Fluorescence spectra were recorded on a SAFAS Spectrofluorometer.

**Dynamic light scattering (DLS) and Static light scattering (SLS)** experiments were performed using ALV Laser Goniometer, which consist in 22 mW HeNe linear polarized laser with 632.8 nm wavelength and an ALV-5000/EPP Multiple Tau Digital Correlator with 125 ns initial sampling time. The samples were kept at constant temperature (25.0 °C) during all the experiments. The accessible scattering angle range is from 30° up to 140°. The solutions were introduced into 10 mm diameter glass cells. The minimum sample volume required for the experiment was 1 milliliter. The data acquisition was done with the ALV-Correlator Control Software, and the counting time varied for each sample from 300 s up to 600 s. The  $R_H$  values of the vesicles were obtained by a cumulant and CONTIN analysis. The determination of the  $R_H$  and  $R_G$  was performed respectively by DLS and SLS measurements of solutions containing 1 M of NaCl. Millipore water was thoroughly filtered through 0.1 μm filters and directly employed for the preparation of the solutions.



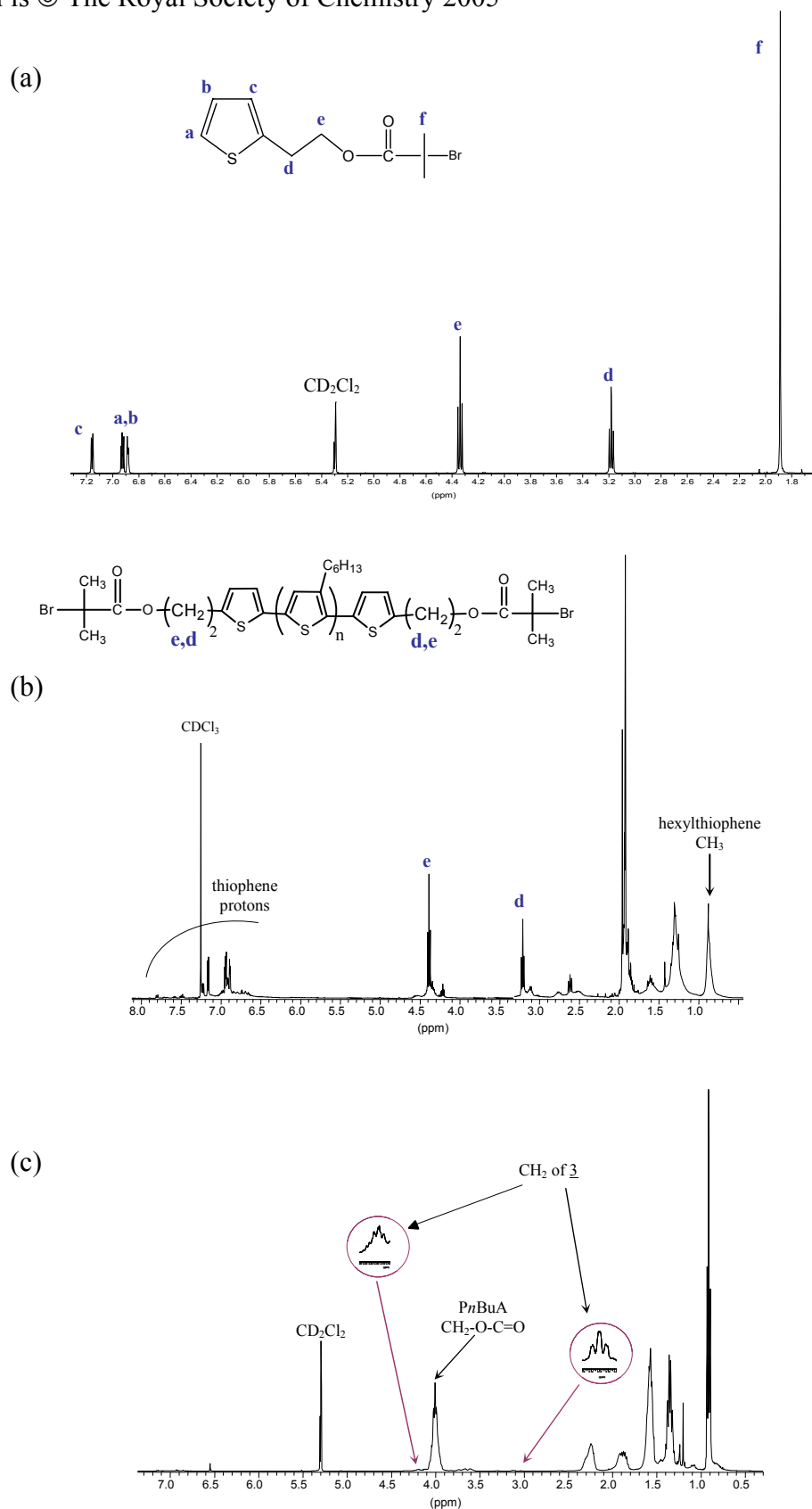
**<sup>1</sup>H NMR analysis:**



S1. (a) <sup>1</sup>H NMR of the initiator **1** (CDCl<sub>3</sub>, 400MHz)

(b) <sup>1</sup>H NMR of the α-(2-thienyl)-PtBuA<sub>35</sub> (CDCl<sub>3</sub>, 400MHz)

(c) <sup>1</sup>H NMR of the PHT<sub>20</sub>-PtBuA<sub>35</sub> (CD<sub>2</sub>Cl<sub>2</sub>, 400MHz)

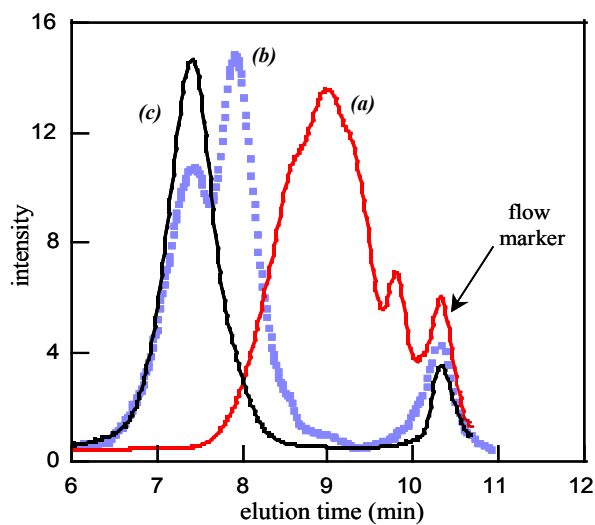


S2. (a)  $^1\text{H}$  NMR of the “blocking agent” (**1'**) ( $\text{CD}_2\text{Cl}_2$ , 400MHz) ;

(b)  $^1\text{H}$  NMR of Br-PHT<sub>12</sub>-Br (**3**) ( $\text{CDCl}_3$ , 400MHz) ;

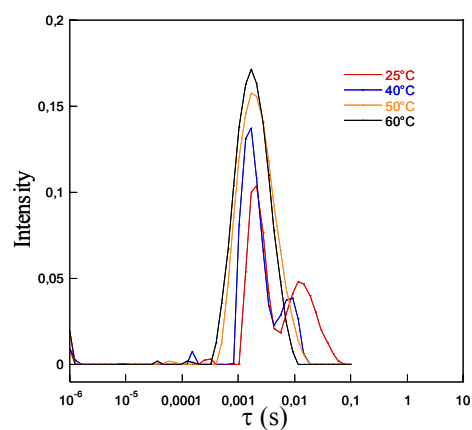
(c)  $^1\text{H}$  NMR of PnBuA<sub>54</sub>-PHT<sub>12</sub>-PnBuA<sub>54</sub> ( $\text{CD}_2\text{Cl}_2$ , 400MHz)

### SEC analysis of the triblock copolymers



**S3.** SEC (eluant THF): **(a)** Br-PHT<sub>12</sub>-Br (*red*); **(b)** PnBuA<sub>54</sub>-PHT<sub>12</sub>-PnBuA<sub>54</sub> before purification (*blue*); **(c)** PnBuA<sub>54</sub>-PHT<sub>12</sub>-PnBuA<sub>54</sub> after purification (*black*).

**Self-assembly study of the PHT<sub>20</sub>-PtBuA<sub>35</sub>.**



**S4.** DLS investigation of the PHT<sub>20</sub>-PtBuA<sub>35</sub> in cyclohexane (C = 2.5 g/L). Evolution of the relaxation time with the temperature.