Electronic Supplementary Information

Quasi-block copolymer libraries on demand via sequential RAFT polymerization in an automated parallel synthesizer

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Example for the determination of the content of BMA monomer in the second block of the copolymers (in PMMA block) for P(BMA-*qb*-MMA) 2A in Table 2.II.

The amount of unreacted monomer for the synthesis of a PBMA macroRAFT agent can be determined from the conversion (as determined by ^{1}H-NMR, Figure S1) and the initial amount of monomer in the reactor. For PBMA macroRAFT agent 2 (Table 1), this is: 1.90×10^{-3} mol of unreacted BMA (*i.e.*, 1.46×10^{-2} mol {initial BMA (excluding the aliquot of 200 μL of reaction mixture for ^{1}H-NMR and SEC characterization)} × [1 – 0.87 {conversion}]).

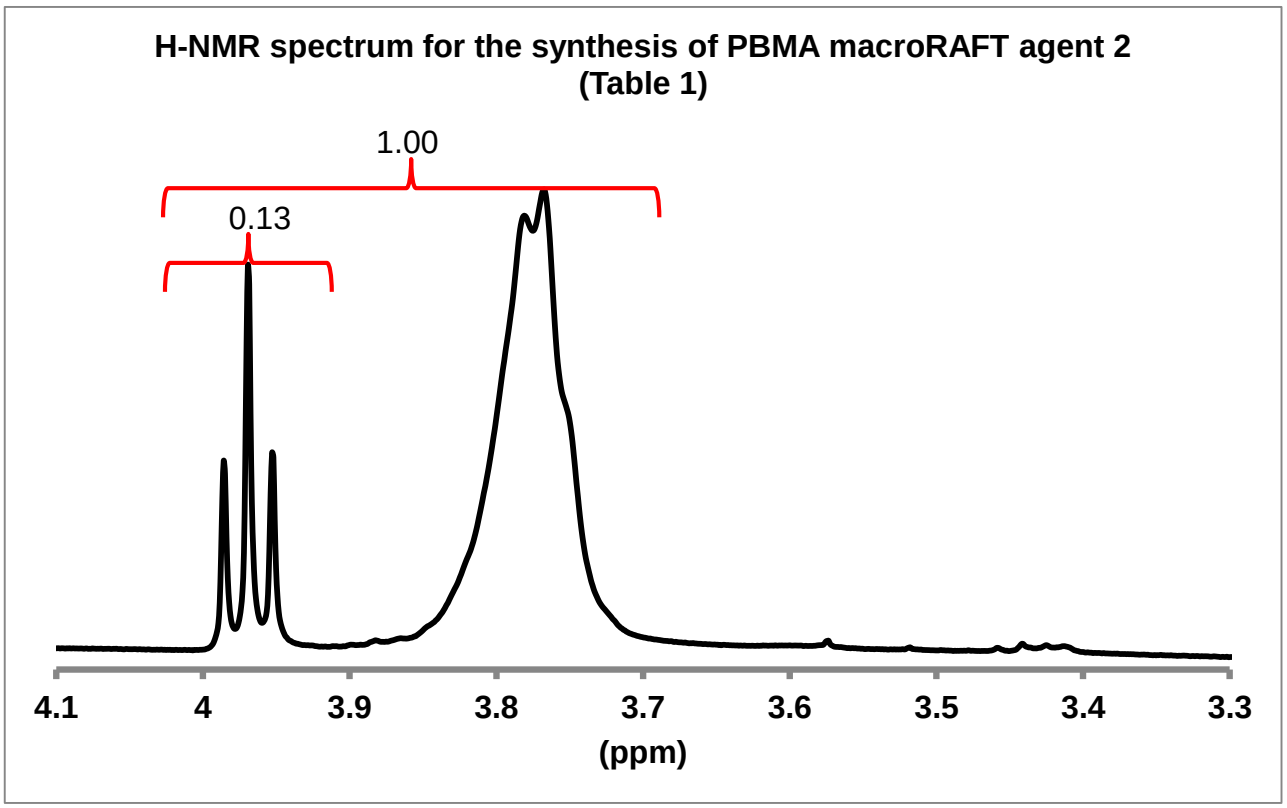

Figure S1. ^{1}H-NMR spectrum of the final reaction mixture of the synthesis of PBMA macroRAFT agent 2 of Table 1.

Next, the unreacted amount of monomer is divided by 5 as the original PBMA macroRAFT agent reaction mixture is split in 5 equal amounts in different reactors. In the discussed example, this leads to 3.80×10^{-4} mol of unreacted BMA per reactor.

The conversion of BMA in the second polymerization step (during the synthesis of the P(BMA-*qb*-MMA)) can be estimated from the normalized integrals of the signals of BMA monomer (around 3.95 ppm) in the ^{1}H-NMR spectra of the macroRAFT agent (Figure S1) and of the P(BMA-*qb*-MMA) (Figure S2) reaction mixtures. In the discussed example and based on the information of Figures S1 and S2, this leads to a conversion value of 0.15 (*i.e.*, {0.13 – 0.11} / 0.13) for BMA in the second polymerization step. With this conversion value and the initial amount of BMA calculated above for

the second polymerization step, the amount of BMA consumed in the second polymerization step can be determined. In the discussed example, this leads to 5.69×10^{-5} mol of BMA (*i.e.*, 3.80×10^{-4} mol {initial BMA} × 0.15 {conversion}) consumed in the second polymerization step.

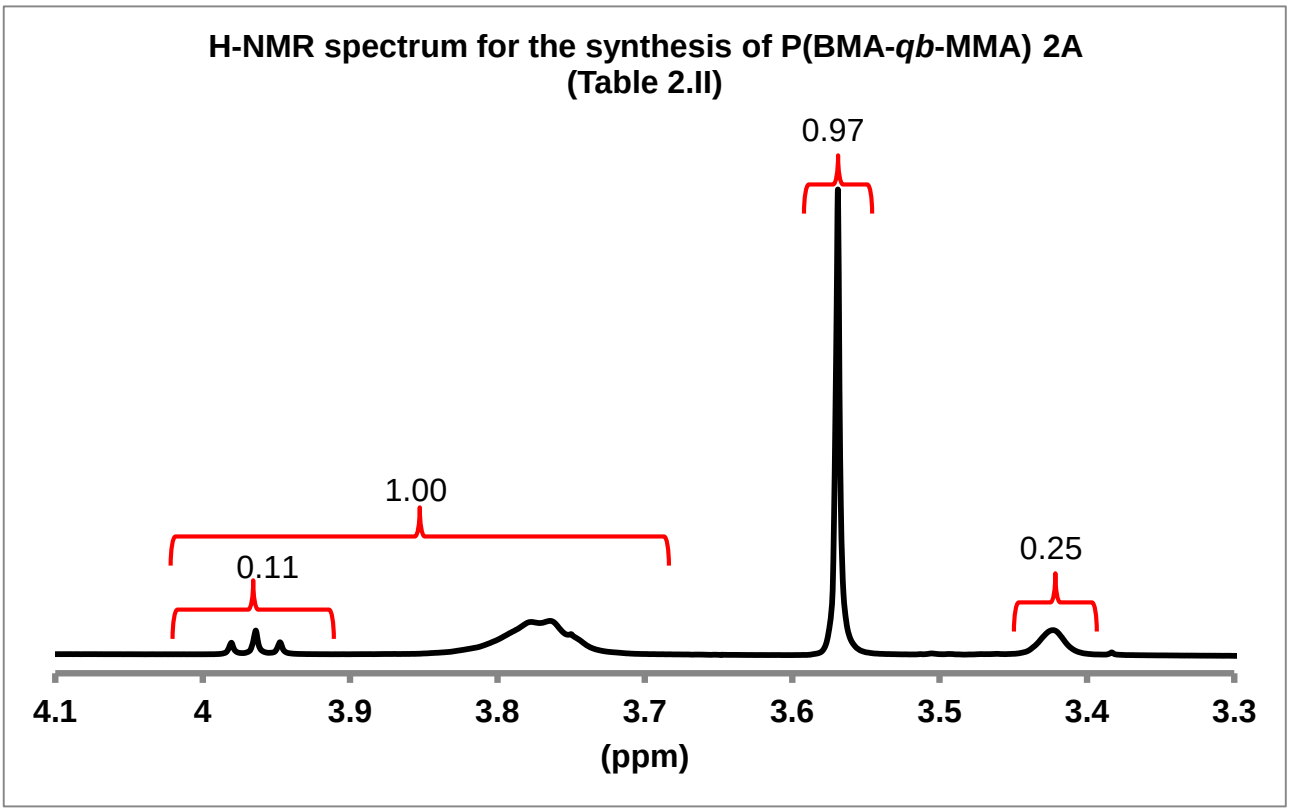

Figure S2. ^{1}H-NMR spectrum of the final reaction mixture of the synthesis of P(BMA-*qb*-MMA) 2A of Table 2.

The conversion of MMA in the second polymerization step (during the synthesis of the P(BMA-*qb*-MMA)) can also be estimated from the normalized integrals of the signals of MMA monomer (around 3.57 ppm) and corresponding PMMA polymer (around 3.42 ppm) in the ^{1}H-NMR spectrum of the P(BMA-*qb*-MMA) (Figure S2) reaction mixture. In the discussed example and based on the information of Figure S2, this leads to a conversion value of 0.20 (*i.e.*, 0.25 / {0.25 + 0.97}) for MMA in the second polymerization step. With this conversion value and the initial amount of MMA utilized the second polymerization step (0.3 mL of MMA corresponds to 2.82×10^{-3} mol of MMA), the amount of MMA consumed in the second polymerization step can be determined. In the discussed example, this leads to 5.64×10^{-4} mol of MMA (*i.e.*, 2.82×10^{-3} mol {initial MMA} × 0.20 {conversion}) were consumed in the second polymerization step.

Finally, the mol % of BMA incorporated into the PMMA block can be estimated with the two amounts of BMA and MMA monomers consumed during the second polymerization step. In the discussed example, this leads to 9 mol % of BMA monomer units (*i.e.*, [5.69×10^{-5} mol of BMA / {5.69×10^{-5} mol of BMA + 5.64×10^{-4} mol of MMA}] × 100) are incorporated into the PMMA block.