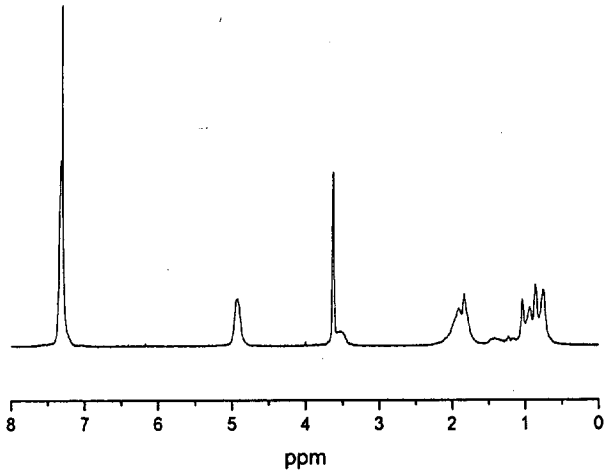
## Supplementary Information




**S1**

$^1$H NMR of final copolymer PMMA-*block*-P(BzMA-*co*-MMA).

**Derivation of Equation to calculate average number molar mass of poly(MMA-b-(MMA-co-BzMA) grown of modified Wang resin:**

The $M_{n,\ 1st\ block}$ is calculated experimentally from the empirical equation. For the $M_{n,\ 2nd\ block}$ we need the molar masses of the two monomers, i.e. $MW_{MMA}$ and $MW_{BzMA}$, the mole fraction of MMA in the 2nd stage feed, i.e., $f_{MMA}$, and the degree of polymerization of the second block, i.e. $DP_{2nd\ block}$:

**Eq.1**

$$M_n = M_{n,exp} + DP_{2nd\,block}\left(f_{MMA}\,MW_{MMA} + \left(1 - f_{MMA}\right)MW_{BzMA}\right)$$

$DP_{2nd\ block}$ is calculated from the cumulative mole fraction of MMA in the copolymer, using, thereby assuming the absence of monomer composition drift:

**Eq.2**

$$F_{MMA} = \frac{DP_{1st\,block} + f_{MMA}\,DP_{2nd\,block}}{DP_{1st\,block} + DP_{2nd\,block}}$$

This can be rearranged to:

**Eq.3**

$$DP_{2nd\,block} = \frac{DP_{1st\,block}\left(1 - F_{MMA}\right)}{F_{MMA} - f_{MMA}}$$

$DP_{1st\ block}$ equals $M_{n,\ exp}/MW_{MMA}$ and substitution in the above equation yields:

**Eq.4**

$$DP_{2nd\,block} = \frac{\frac{M_{n,exp}}{MW_{MMA}}\left(1 - F_{MMA}\right)}{F_{MMA} - f_{MMA}}$$

Substitution of **Eq.4** in **Eq.1** finally yields:

$$M_n = M_{n,exp} + \frac{\frac{M_{n,exp}}{MW_{MMA}}\left(1 - F_{MMA}\right)}{F_{MMA} - f_{MMA}}\left(f_{MMA}\,MW_{MMA} + \left(1 - f_{MMA}\right)MW_{BzMA}\right)$$