Supporting Information

# RAFT macro-surfmers and their use in the ab initio RAFT emulsion polymerization to decouple NP size and polymer MW

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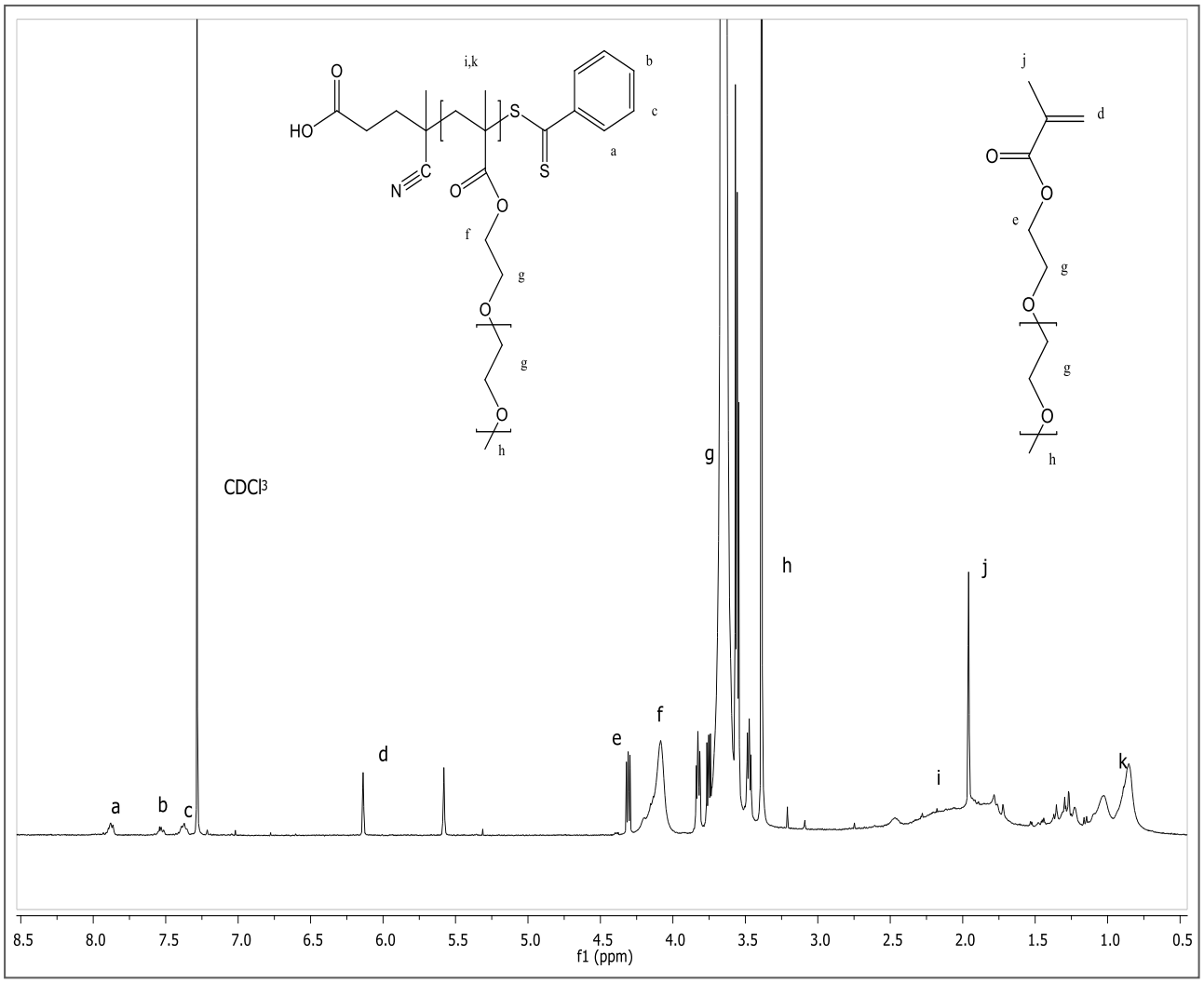


**Figure S1:** $^{1}$H NMR spectrum of the sample 20PEGMA after 24h of reaction

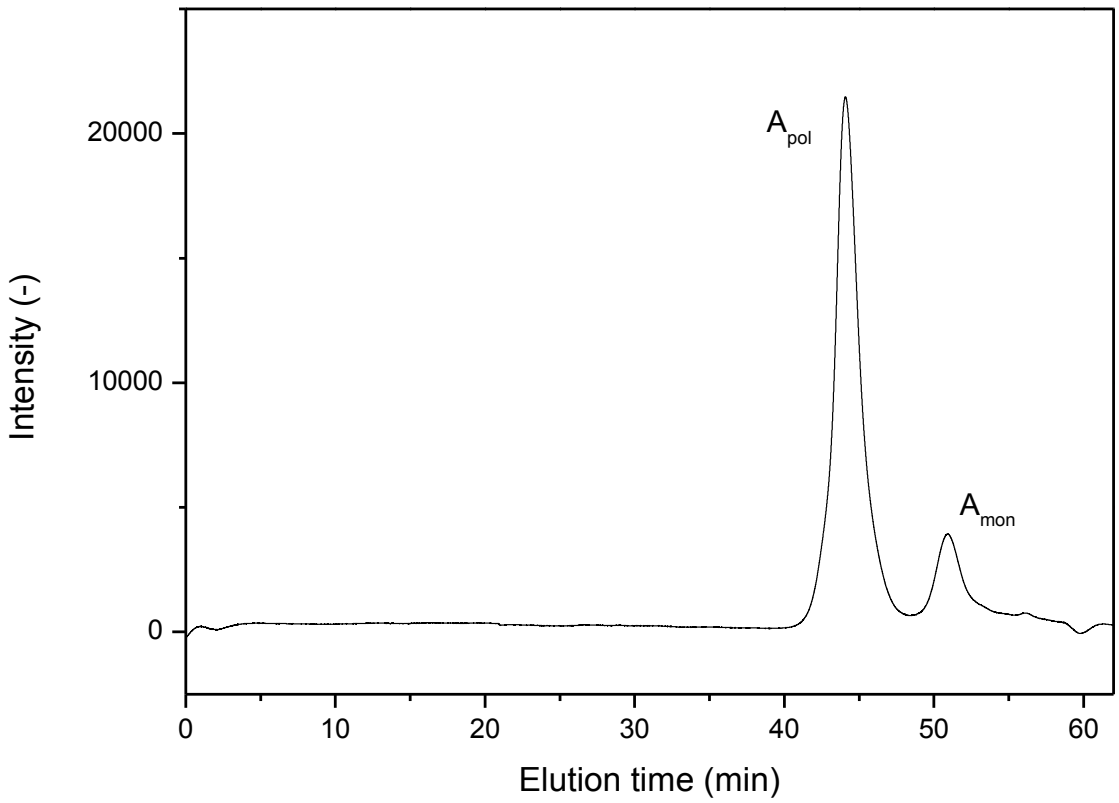


**Figure S2:** GPC trace of the sample 20PEGMA after 24h of reaction

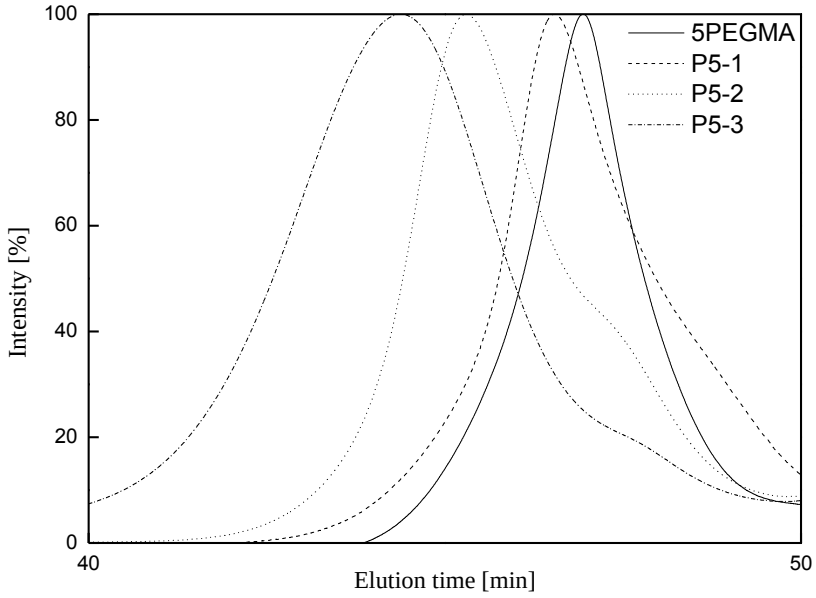


**Figure S3:** GPC traces of the block copolymers produced with 5PEGMA in the AIREP experiments P5-1, P5-2 and P5-3 in **Table 3**

**List of abbreviations**

| | |
|---|---|
| $A_{Cov}$ | NP surface area that a single hydrophilic chain can cover |
| $C_{b\_hydro}$ | Hydrophilic chain weight concentration |
| $C_{lipo}$ | Lipophilic monomer weight concentration |
| $Dn$ | NP diameter |
| $DP_{hydro}$ | Degree of polymerization of the hydrophilic block |
| $DP_{lipo}$ | Degree of polymerization of the lipophilic block |
| $DP_{ratio}$ | Ratio between $DP_{lipo}$and $DP_{hydro}$ |
| $MW_{cop}$ | Molecular weight of the block-copolymer that constitutes the NP |
| $MW_{b\_hydro}$ | Molecular weight of the hydrophilic chain (macro-RAFT surfmers in this work) |
| $MW_{hydro}$ | Molecular weight of the hydrophilic monomer (PEGMA in this work) |
| $MW_{lipo}$ | Molecular weight of the lipophilic monomer (MMA in this work) |
| $MW_{RAFT\_agent}$ | Molecular weight of the RAFT agent (CPA in this work) |
| $N_{Avo}$ | Avogadro number |
| $N_{b\_hydro}$ | Number of hydrophilic chains located on the NP surface |
| $n_{lipo}$ | Initial number of moles of the lipophilic monomer |
| $N_{NPs}$ | Number concentration of NPs in the system |
| $n_{RAFT\_agent}$ | Initial number of moles of the RAFT agent |
| $V$ | Volume of the mixture |
| $\rho_{b\_lipo}$ | Density of lipophilic chains that form the NP core (pMMA in this work) |

**Derivation of equation (12) from equations (8-11)**

$$MW_{cop} = MW_{hydro} \cdot DP_{hydro} + MW_{lipo} \cdot DP_{lipo} + MW_{RAFT\_agent} \quad (8)$$

$$A_{Cov} = \frac{\pi \cdot Dn^2}{N_{b\_hydro}} \quad (9)$$

$$N_{b\_hydro} = \frac{C_{b\_hydro} \cdot N_{Avo}}{MW_{b\_hydro} \cdot N_{NPs}} \quad (10)$$

$$N_{NPs} = \frac{6 \cdot C_{lipo}}{\pi \cdot Dn^3 \cdot \rho_{b\_lipo}} \quad (11)$$

Combining equations (9-11), it is possible to obtain equation (12a):

$$A_{Cov} = \frac{\pi \cdot Dn^2}{\frac{C_{b\_hydro} \cdot N_{Avo}}{MW_{b\_hydro} \cdot N_{NPs}}} = \frac{\pi \cdot Dn^2}{\frac{C_{b\_hydro} \cdot N_{Avo}}{MW_{b\_hydro} \cdot \frac{6 \cdot C_{lipo}}{\pi \cdot Dn^3 \cdot \rho_{b\_lipo}}}} = \frac{6 \cdot C_{lipo} \cdot MW_{b\_hydro}}{C_{b\_hydro} \cdot N_{Avo} \cdot Dn \cdot \rho_{b\_lipo}} \quad (12a)$$

$C_{lipo}$ and $C_{b\_hydro}$ can be expressed as:

$$C_{lipo} = \frac{n_{lipo} \cdot MW_{lipo}}{V} \quad (12b)$$

$$C_{b\_hydro} = \frac{n_{b\_hydro} \cdot MW_{b\_hydro}}{V} \quad (12c)$$

where V is the volume of the mixture and $n_{b\_hydro}$ and $n_{lipo}$ are the initial number of moles of the hydrophilic chain and of the lipophilic monomer, respectively. In the case of well controlled RAFT polymerization (eq. (8) is true), the RAFT functional end group is present at the end of each chain and, for this reason, $DP_{lipo}$ can be expressed as:

$$DP_{lipo} = \frac{n_{lipo}}{n_{RAFT\_agent}} = \frac{n_{lipo}}{n_{b\_hydro}} \quad (12d)$$

Where $n_{RAFT\_agent}$ is the initial number of moles of the RAFT agent.

If we combine equations (12b,c,d) with equation (12a), it is possible to obtain:

$$Dn = \frac{6 \cdot n_{lipo} \cdot MW_{lipo}}{N_{Avo} \cdot A_{Cov} \cdot \rho_{b\_lipo} \cdot n_{b\_hydro}} = \frac{6 \cdot DP_{lipo} \cdot MW_{lipo}}{N_{Avo} \cdot A_{Cov} \cdot \rho_{b\_lipo}} \quad (12)$$