## **Supplementary information**

# Fast and facile one-step synthesis of monodisperse thermo-responsive core-shell microspheres and applications

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#### <sup>1</sup>HNMR spectra for the Synthesis of P(mPEGA-co-MEA)-b-PAA-TTC Macro-RAFT agent.



**Fig. S1** <sup>1</sup>HNMR spectra of the reaction mixture before and after 24h reaction for the Synthesis of P(mPEGA-*co*-MEA)-*b*-PAA-TTC Macro-RAFT agent. The disappearance of the double band signals reveals all the monomers were consumed in the polymerization



Fig. S2 <sup>1</sup>HNMR spectra of P(mPEGA-co-MEA)-TTC-2

#### 1. Particle growth in the absence of DDMAT



**Fig. S3** SEM images of PMMA particles prepared by photoinitiated RAFT dispersion polymerization of MMA with 15 wt% P(mPEGA-*co*-MEA)-TTC-2 and without DDMAT at irradiation time marked on the images.

#### 3. Effect of photoinitiator concentration

An exponent of 0.39 for the dependence of particle diameter on photoinitiator concentration was predicted by Paine's theoretical analysis (*Macromolecules* **1990**, *23* (12), 3109-3117). The exponent of 0.14 obtained in this work (Figure S1) is obviously lower than the theoretical predicted value, suggesting that the particle diameter is not as sensitive to the photoinitiator concentration as it is in conventional dispersion polymerization.



**Fig. S4** Double logarithmic plots of weight–average diameter versus photoinitiator concentration photoinitiated RAFT dispersion polymerization of MMA in the presence of 0.25 wt % DDMAT.

#### 4. Effect of monomer concentration



**Fig. S5** SEM images of PMMA microspheres obtained by photoinitiated RAFT dispersion polymerization of MMA with different different MMA concentrations (marked on the images) in the presence of 15 wt % P(mPEGA-*co*-MEA)-TTCs and 0.25 wt % DDMAT.

#### 5. Effect of ethanol/water ratio

Monodisperse PMMA microspheres were obtained at ethanol content ranging from 40 wt% to 50 wt%. Meanwhile, only a gelatinous mixture was formed at ethanol content up to 55 wt%, which can be attributed to the excessive solubility of PMMA in the dispersion medium.

P(mPEGA-co-MEA)-TTC-1:



P(mPEGA-co-MEA)-TTC-2:



P(mPEGA-co-MEA)-TTC-3:



**Fig S6** SEM images of PMMA microspheres obtained by photoinitiated RAFT dispersion polymerization of MMA with different ethanol/water ratios (wt/wt, marked on the images) in the presence of 15 wt % P(mPEGA-co-MEA)-TTCs and 0.25 wt % DDMAT.

#### 6. Other results for P(mPEGA-co-MEA)-TTC-1 and P(mPEGA-co-MEA)-TTC-3



**Fig. S7** SEM images of PMMA microspheres obtained by photoinitiated RAFT dispersion polymerization of MMA with different P(mPEGA-co-MEA)-TTC-1 concentrations (wt %, marked on the images) in the presence of 0.25 wt % DDMAT.



**Fig. S8** SEM images of PMMA microspheres obtained by photoinitiated RAFT dispersion polymerization of MMA with different P(mPEGA-co-MEA)-TTC-3 concentrations (wt %, marked on the images) in the presence of 0.25 wt % DDMAT.



Fig. S9 SEM images of PMMA microspheres obtained photoinitiated RAFT dispersion by polymerization of MMA with different photoinitiator concentration (wt %, marked on the in the presence images) of 15 wt % P(mPEGA-co-MEA)-TTC-1 and 0.25 wt % DDMAT



Fig. S10. SEM images of PMMA microspheres obtained by photoinitiated RAFT dispersion different polymerization of MMA with photoinitiator concentration (wt %, marked on the images) in the presence of 15 wt % P(mPEGA-co-MEA)-TTC-3 and 0.25 wt % DDMAT

### 7. Equations of $d_n$ , $d_w$ and the particle number $(N_p)$

$$d_{n} = \sum_{i=1}^{n} n_{i} d_{i} / n;$$
$$d_{w} = (\sum_{i=1}^{n} n_{i} d_{i}^{4}) / (\sum_{i=1}^{n} n_{i} d_{i}^{3})$$

where  $n_i$  is the number of particles with diameter  $d_i$ .

The particle number  $(N_p)$  was calculated by  $N_p = \frac{W_0 Y}{\rho V_n}$ , where  $W_0$  is the feeding weight of monomers, *Y* the particle yield, and  $\rho$  the density of PMMA,  $V_n$  the number-average volume of particles  $(V_n = \sum_{i=1}^n n_i V_i / n = \frac{\pi}{6} \sum_{i=1}^n n_i D_i^3 / n)$ .