

Supplementary Information

Monodisperse Highly Cross-linked “Living” Microspheres Prepared via Photoinitiated RAFT Dispersion Polymerization

Jianbo Tan, Xin Rao, Jianwen Yang, and Zhaohua Zeng*

Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, and Key Laboratory of Designed Synthesis and Application of Polymer Material, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China

About photoinitiated RAFT dispersion polymerization

There exist two types of dispersion polymerization currently. The classical dispersion polymerization, developed in 1975, involves in the precipitation of polymer chains from the homogeneous system, nucleation via coalescence of the precipitated chains, stabilization of the particles by absorbing the stabilizer, and growth of the particles, forming submicron- or micron-sized spherical particles (**normally 1–15 μm**). Recently another version of dispersion polymerization is developed by Prof. Z. S. An, Prof. S. P. Armes, and Prof. C. Y. Pan *et al.*. It involves **self-assembly of the block copolymers** generated in the homogeneous system via RAFT polymerization, forming various kinds of **nano-sized** micelles or vesicles (Polym. Chem., 2013, 4, 873–881, a review article on this field). Our procedure, photoinitiated RAFT dispersion polymerization, essentially belongs to the classical dispersion polymerization rather than the extended version, although a RAFT process is involved in the procedure.

The RAFT agent in photoinitiated RAFT dispersion polymerization primarily controls the nucleation stage to a reasonable time scale and contributes to the formation of the big spheres which act as a reservoir for the controlled polymer chains and provide a buffering effect to the nucleation (*Macromolecules*, 2012, 45, 8790–8795). It is noticed that a well-controlled process is not preferable for preparing monodisperse microspheres, because the excessive control of

polymerization will distribute the nucleation. Using a higher amount of RAFT agent or lower photoinitiator concentration may achieve better control effect of the polymerization, but this will lead to low particle yield and broad particle size distribution. After all, the primary objective of the photoinitiated RAFT dispersion polymerization strategy is to synthesize monodisperse functional microspheres readily, rather than to control the molecular weight. In addition to photoinitiation, the RAFT process is necessary and crucial in our procedure, although it is not a fully controlled process. Therefore, we call the procedure “photoinitiated RAFT dispersion polymerization”.

Other supplementary information

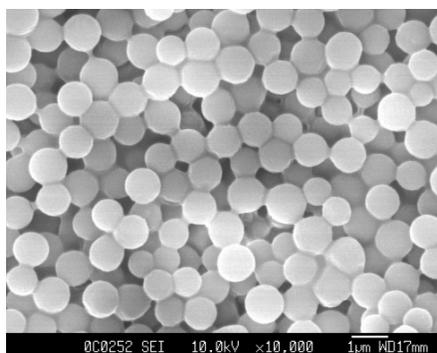


Fig. S1 SEM image of PMMA microspheres prepared by photoinitiated dispersion polymerization of MMA in the absence of any RAFT agent with 2 wt % DPGDA.

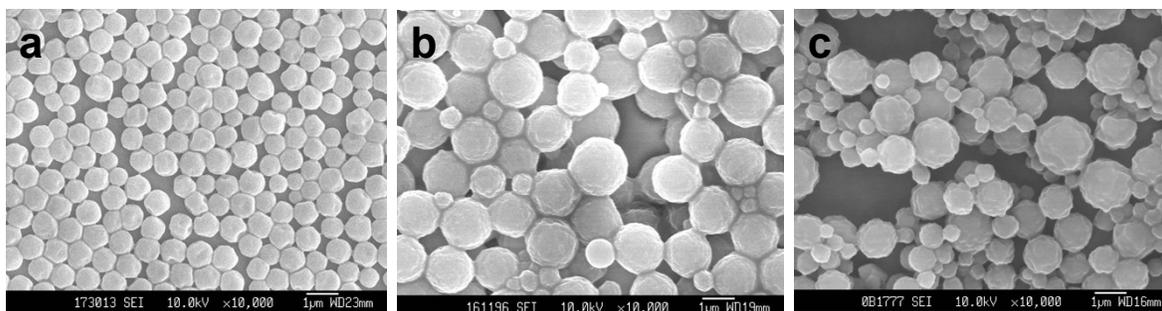
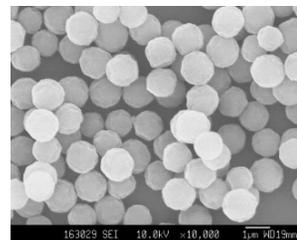
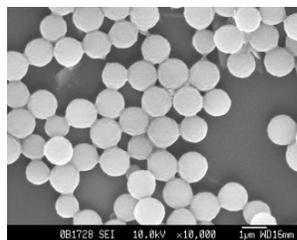


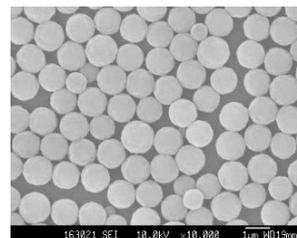
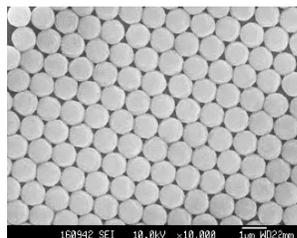
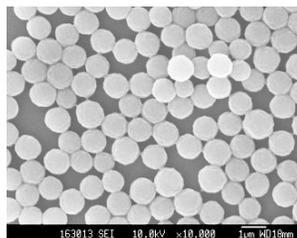
Fig. S2 SEM images of PMMA microspheres prepared by photoinitiated RAFT dispersion polymerization with (a) 0.5 wt % BDMAT + 5 wt % DPGDA + 1 wt % D 1173; (b) 1.0 wt % BDMAT + 15 wt % DPGDA; (c) 0.5 wt % BDMAT + 4 wt % TMPTA.

10 wt % DPGDA

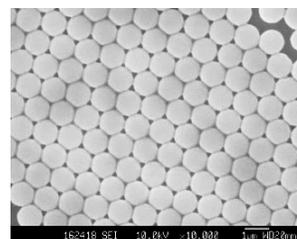
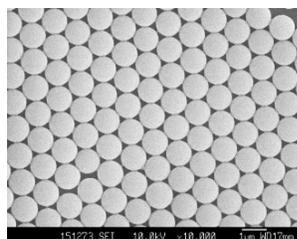
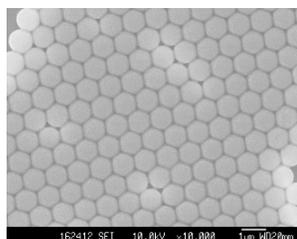
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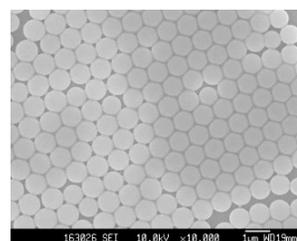
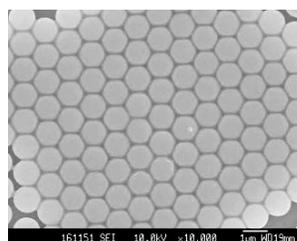
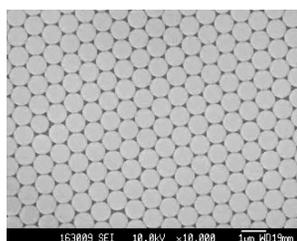
5 wt % DPGDA



2 wt % DPGDA



1 wt % DPGDA



0.25 wt % BDMAT

0.5 wt % DDMAT

1.0 wt % DDMAT

Fig. S3 SEM images of PMMA microspheres prepared by photoinitiated RAFT dispersion polymerization with different DPGDA concentrations and different BDMAT concentrations.

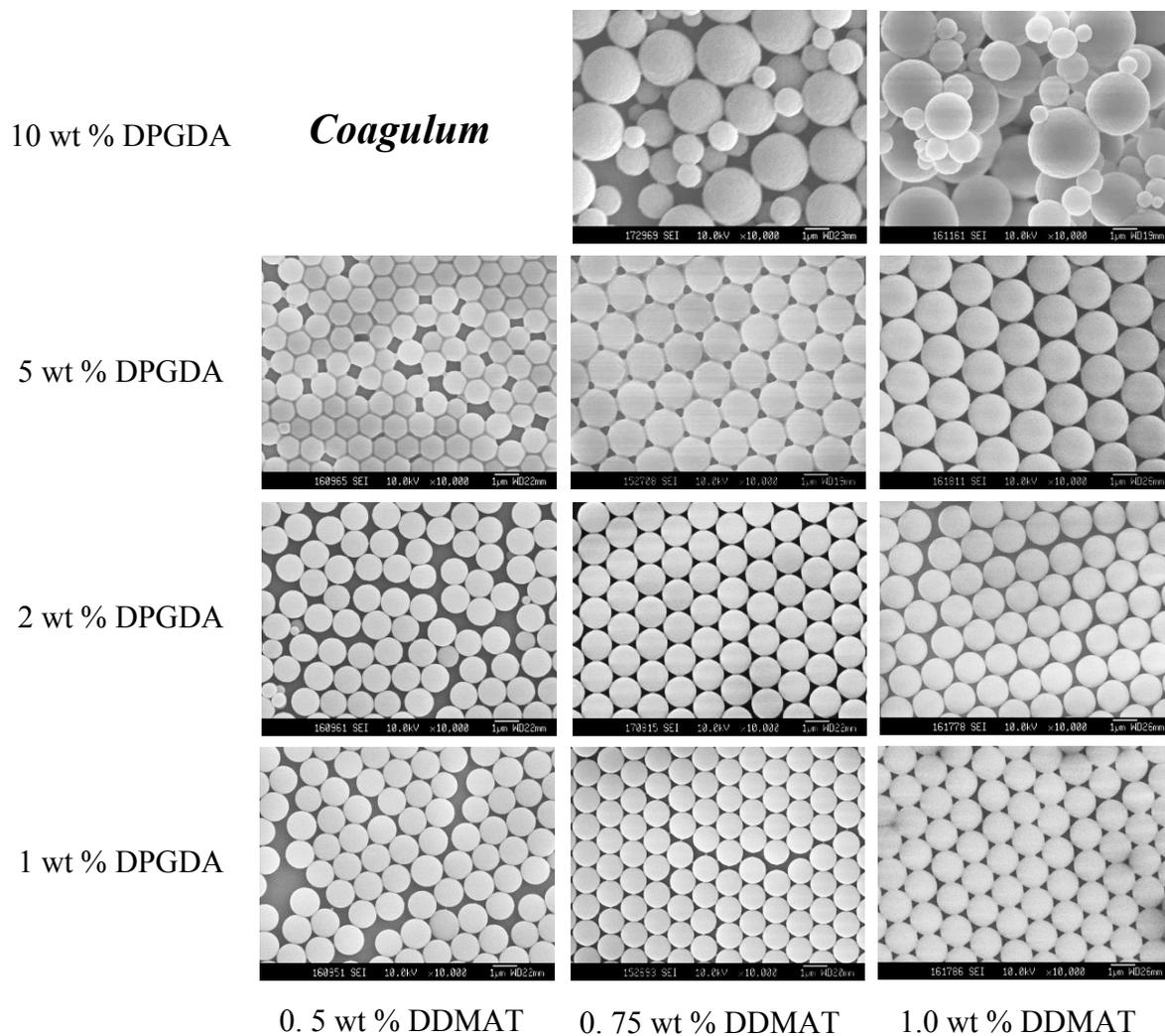


Fig. S4 SEM images of PMMA microspheres prepared by photoinitiated RAFT dispersion polymerization with different DPGDA concentrations and different DDMAT concentrations.

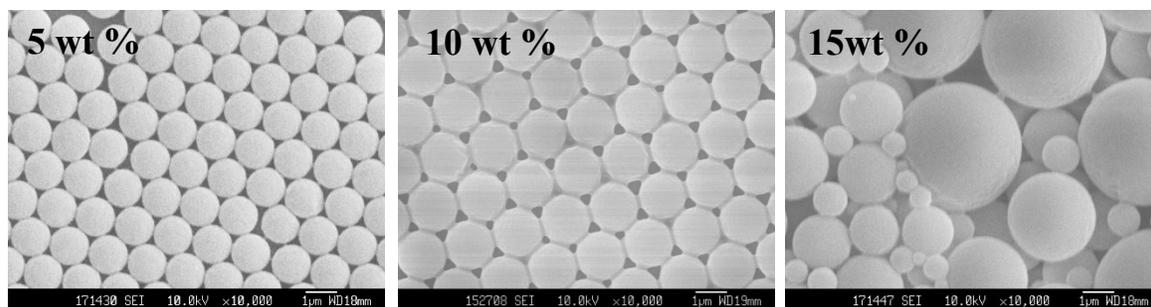


Fig. S5 SEM image of PMMA microspheres prepared by photoinitiated dispersion polymerization of MMA in the presence of 0.75 wt % DDMAT and 5 wt % DPGDA with MMA concentrations marked on the images.