Monodisperse Poly(methyl methacrylate) Microspheres with Tunable Carboxyl Group on the Surface Obtained by Photoinitiated RAFT Dispersion Polymerization

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EXPERIMENTAL SECTION

Materials

Methyl methacrylate (MMA, Aladdin) was passed through a column of basic alumina (Aladdin) prior to storage under refrigeration at 4 °C. Acrylic acid (AA, Aladdin), ammonium carbonate ((NH₄)₂CO₃, 3A Chemistry), poly (ethylene glycol) methyl ether acrylate (PEGA, 480 g/mol, Sigma-Aldrich), calcium chloride (CaCl₂, Aladdin), europium (III) Chloride Hexahydrate (EuCl₃·6H₂O, Aladdin), sodium fluoride (NaF, Aladdin), lanthanum(III) chloride heptahydrate (LaCl₃·7H₂O, Aladdin), and 2,2-dimethyl-2-phenylacetophenone (HMPP, Aladdin) were used without further purification. 2,2-Azobisisobutyronitrile (AIBN, Aladdin) was recrystallized from ethanol prior to storage under refrigeration at 4 °C, The RAFT agent S-1-dodecyl-S'-(α , α '-dimethyl- α "-acetic acid) trithiocarbonate (DDMAT) was synthesized using a published procedure^[1].

Characterization

Transmission Electron Microscopy (TEM). The obtained dispersions were diluted 100-fold with water. A drop of the solution was placed on the copper grip for 1 min and then blotted with filter paper to remove excess solution. TEM observations were carried out on a Hitachi 7700 Spirit instrument operated at 120 kV.

Gel Permeation Chromatography (GPC). The molecular weight and polydispersity of the block copolymers were measured by gel permeation chromatography (GPC) using a Waters 1515 GPC instrument with dimethylformamide (DMF) as the mobile phase and Waters styragel HR1, HR4 columns. The eluent was HPLC grade DMF containing 10 mM LiBr and was filtered prior to use. The flow rate of DMF was 1.0 mL/min. Linear poly (methyl methacrylate) polymers with narrow molecular weight distributions were used as the standards to calibrate the apparatus.

¹*H NMR Spectroscopy*. Nuclear magnetic resonance (NMR) spectra were recorded in DMSO- d_6 using a Bruker Avance III 400 MHz NMR spectrometer at a temperature of 25 °C.

Scanning electron microcopy (SEM). SEM images were collected using a Hitachi SU8010 (Tokyo, Japan) electron microscope on samples sputter-coated with gold prior

imaging. The sample for SEM imaging was prepared by drop casting the diluted dispersion on a clean mica films and drying at room temperature prior to sputter-coating. SEM images were analyzed by using the software program named Image pro Plus 6.0. The average diameter (d_n) and coefficient of variation of diameter (C_v) were calculated according to the following equations:

$$d_n = \sum_{i=1}^n \mathbf{d}_i / n \tag{S1}$$

$$C_{\rm v} = \sqrt{\frac{\sum_{i=1}^{n} (d_i - d_n)^2}{n - 1}} / d_n$$
(S2)

X-ray diffraction (XRD). XRD spectras were recorded on a D/MAX-Ultima IV X-Ray Diffractometer in the 2θ range of 5-75 °. Each dried LaF₃:Eu/PMMA composites in advance was ground to from a fine powder.

Thermogravimetric analysis (TGA). TGA was performed using a STA449F5 instrument under a stream of nitrogen. The dried LaF₃:Eu/PMMA composites were heated from 25 to 600 °C with a heating rate of 10 °C/min.

Focused Ion Beam Filed Emission Scanning Electron Microscope (FIB-SEM). FIB-SEM images were collected using a Tescan LYRA 3XMU electron microscope on samples sputter-coated with gold prior imaging. The samples of occlusion experiment were washed three times with deionized water followed by three rinses with ethanol, finally dried at room temperature overnight prior to sputter-coating.

Synthesis of PAA₈₆-DDMAT

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The synthesis of PAA₈₆-DDMAT is given below: AA (20.0 g, 0.28 mol), DDMAT (1.0120 g, 2.78 mmol), AIBN (0.0912 g, 0.56 mmol), trioxane (2.498 g, 0.028 mol), and 1,4-Dioxane (113.3 g) were weighted into a 250 ml round bottom flask and purged with nitrogen for 1 h. The flask was then immersed into a preheated oil bath at 70 °C for 3.5 h (Monomer conversion = 86 % as judged by ¹H NMR). The polymerization was then quenched by immersion in ice water and exposure to air. The polymer was

precipitated by pouring into n-hexane (300 mL) and washed several times with additional n-hexane. The obtained product was dried at 45 °C under vacuum overnight, and then a mean degree of polymerization of 86 for this macro-CTA (PAA₈₆-DDMAT).

Synthesis of PPEGA33-CTA

The synthesis of PPEGA₃₃-DDMAT is given below: PEGA (20.0 g, 0.042 mol), DDMAT (0.4341 g, 1.19 mmol), AIBN (0.0391 g, 0.24 mmol), trioxane (0.375 g, 0.004 mol), and 1,4-Dioxane (30.0 g) were weighted into a 250 ml round bottom flask and purged with nitrogen for 1 h. The flask was then immersed into a preheated oil bath at 70 °C for 4.5 h (Monomer conversion = 95% as judged by ¹H NMR). The polymerization was then quenched by immersion in ice water and exposure to air. The polymer was precipitated by pouring into n-hexane (300 mL) and washed several times with additional n-hexane. The obtained product was dried at 45 °C under vacuum overnight, and then a mean degree of polymerization of 33 for this macro-CTA (PPEGA₃₃-DDMAT).

Photoinitiated RAFT Dispersion Polymerization of MMA using PAA₈₆-DDMAT as the macro-CTA

In a typical experiment, MMA (2.0 g, 10 wt % relative to the reaction mixture), PAA₈₆-DDMAT (0.1 g, 5 wt % relative to MMA), DDMAT (0.005 g, 0.25 wt % relative to MMA), and HMPP (0.08 g, 4 wt % relative to MMA) were dissolved in an ethanol/water (7.2 g/10.8 g) mixture. The reaction mixture was purged with nitrogen for 20 min, sealed, and then irradiated with a LED lamp (365 nm, 11.5 mW/cm²) at room temperature for 2 h. The sample was purified by three cycles of centrifugation-redispersion in ethanol/water (40/60, w/w) and finally dispersed in water for further use. Details of polymerizations were shown in table S1.

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	Entry	MMA	PAA86-	HMPP	DDMAT	Ethanol/water			
_	Number	(g)	DDMAT(g)	(g)	(g)	(g/g)			
-	1	2.0	0.02	0.08	0.005	7.2/10.8			
	2	2.0	0.04	0.08	0.005	7.2/10.8			
	3	2.0	0.1	0.08	0.005	7.2/10.8			
	4	2.0	0.15	0.08	0.005	7.2/10.8			
	5	2.0	0.2	0.08	0.005	7.2/10.8			

Table S1. Recipes for ptotoinitiated RAFT dispersion polymerization of MMA using PAA_{86} -DDMAT as macro-CTA.

Photoinitiated RAFT dispersion polymerization of MMA using binary mixtures of PAA86-DDMAT and PPEGA33-DDMAT

MMA (2.0 g, 10 wt % relative to the reaction mixture), DDMAT (0.005 g, 0.25 wt % relative to MMA), PAA₈₆-DDMAT and PPEGA₃₃-DDMAT (total amount was 0.1 g, 5 wt % relative to MMA), and HMPP (0.08 g, 4 wt % relative to MMA) were dissolved in an ethanol/water (7.2 g/10.8 g) mixture. The weight ratios of PAA₈₆-DDMAT and PPEGA₃₃-DDMAT were varied in the range of 1/9 to 10/0 (see Table S2). The reaction mixture was purged with nitrogen for 20 min, sealed, and then irradiated with a LED lamp (365 nm, 11.5 mW/cm²) for 2 h at room temperature. The samples were purified by three cycles of centrifugation-redispersion in ethanol/water (40/60, w/w) and finally dispersed in water for further use.

Table S2. Recipes for ptotoinitiated RAFT dispersion polymerization of MMA using PAA₈₆-DDMAT and PPEGA₃₃-DDMAT as macro-CTAs.

Entry	MMA	PAA86-	PPEGA ₃₃ -	HMPP	DDMAT	ethanol/water	
Number	(g)	DDMAT (g)	DDMAT (g)	(g)	(g)	(g/g)	
1	2.0	0.01	0.09	0.08	0.005	7.2/10.8	
2	2.0	0.03	0.07	0.08	0.005	7.2/10.8	
3	2.0	0.05	0.05	0.08	0.005	7.2/10.8	
4	2.0	0.07	0.03	0.08	0.005	7.2/10.8	
5	2.0	0.09	0.01	0.08	0.005	7.2/10.8	

Quantification of carboxyl groups on the surface of PMMA microspheres

Quantification of carboxyl groups on the surface of microspheres by acid-base titration, potentiometric and conductometric titrations were simultaneously carried out in air at room temperature. PMMA microspheres were diluted in distilled water (25.0 g, 1 wt % solids content). A standardized NaOH solution (0.2 - 0.4 mL, 0.1 M) was added, then back-titrated using 0.025 M HCl added in volume increments of 10 or 20

 μ L. In order to ensure the accuracy of the result, each of potentiometric and conductometric titrations was conducted for three times, the final volume of HCl could be the average of these result. A blank titration to correct for CO₂ uptake was carried out by the same way.

The mean number of -COOH groups can be calculated as follows equations.

$$N_{MMA-\text{titr}} = C_{HCl} \times V_{HCl} \times N_A \tag{S3}$$

$$S_{\text{particle}} = 4 \times \pi \times R^2 \tag{S4}$$

$$V_{particle} = \frac{4}{3} \times \pi \times R^3 \tag{S5}$$

$$m_{particle} = \rho \times V_{particle} \tag{S6}$$

$$N_{\text{particle}} = m_{\text{sample}} \times \text{solids content \%} / m_{\text{particle}}$$
 (S7)

$$N_{MMA} / particle = N_{MMA-titr} / N_{particle}$$
 (S8)

$$N_{MMA} / \text{nm}^2 = N_{MMA} / particle / S_{\text{particle}}$$
 (S9)

 $N_{\text{MAA-titr}}$ means the number of -COOH groups to be titrated, R is the mean particle radius, S_{particle} is the mean surface area, V_{particle} is the mean particle volume, ρ is the density of PMMA (ρ =1.19 g/cm³), N_{A} is Avogadro's number, m_{particle} is the mean particle mass, m_{sample} means the mass of sample titrated, N_{particle} is the practical number of PMMA particles in the titrated sample, $N_{\text{MAA}}/particle$ is the number of surface -COOH groups per particle and $N_{\text{MAA}}/\text{nm}^2$ is the number of surface -COOH groups per nm².

Precipitation of calcite crystals in the presence of carboxyl-functionalized PMMA microspheres

An aqueous solution (10 mL) comprising CaCl₂ (2 mM) and 0.05 wt % PMMA microspheres was placed in a 25 mL beaker. Then the 25 mL beaker was put in a 250 mL beaker and sealed. CaCO₃ crystals were precipitated onto a cover glass placed at the bottom of this aqueous solution by exposure to ammonium carbonate vapor (3.0 g, placed at the bottom of the 250 mL Beaker) for 24 h at room temperature. The cover

glass was then removed from the solution and washed three times with deionized water followed by three rinses with ethanol, finally dried at room temperature overnight. Each set of occlusion experiment was performed at least twice and finally consistent results were obtained in each case.

Colloidal stability of the carboxyl-functionalized PMMA microspheres

PMMA microspheres (1 mL, 1 wt % solids content) were frozen at -20 °C in 1.5 mL centrifuge tube, and then allowed to thaw at room temperature. Colloidal stability was evaluated by visual inspection.

PMMA microspheres (100 μ L, 5 wt% solids content) were transferred via a pipet into 1.5 mL centrifuge tubes to which 400 μ L aliquots of various CaCl₂ aqueous solutions were added (0.005 - 0.25 M). Colloidal stability was evaluated by visual inspection.

Synthesis of LaF₃:Eu/PMMA composites

Typically, selected PMMA microspheres (8.0 g, 1 wt % solid content), and an aqueous solution containing $LaCl_3 \cdot 7H_2O$ and $EuCl_3 \cdot 6H_2O$ (5.0 g, 0.05 mmol, La^{3+} : $Eu^{3+} = 95\% : 5\%$) were weighted in a 50 mL round bottom flask and stirred for 30 min. Then a NaF solution (15.0 g, 1.6 mmol) was added dropwise for 30 min. The flask was immersed into a preheated oil bath at 75 °C for 4 h. The samples were purified by several centrifugation-redispersion cycles in water.

ADDITIONAL RESULTS

Table S3. Summary of the colloidal stabilities of carboxyl-functionalized PMMA microspheres prepared by photoinitiated RAFT dispersion polymerization with different macro-RAFT agents.

Complex	CaCl ₂ concentration (mol/L)					Encorre there?	
Samples	0.005	0.025	0.05	0.1	0.15	0.25	Freeze-tnaw ^a
1 wt% PAA ₈₆ -DDMAT (Table S1-1)	\checkmark	×	×	×	×	×	\checkmark
2 wt% PAA ₈₆ -DDMAT (Table S1-2)	\checkmark	×	×	×	×	×	\checkmark
3 wt% PAA ₈₆ -DDMAT (Table S1-3)	\checkmark	×	×	×	×	×	\checkmark
4 wt% PAA ₈₆ -DDMAT (Table S1-4)	\checkmark	×	×	×	×	×	\checkmark
5 wt% PAA ₈₆ -DDMAT (Table S1-5)	\checkmark	×	×	×	×	×	\checkmark
7.5 wt% PAA ₈₆ -DDMAT (Table S1-6)	\checkmark	×	×	×	×	×	\checkmark
PAA ₈₆ /PPEGA ₃₃ 1/9 (Table S2-1)	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark
PAA ₈₆ /PPEGA ₃₃ 3/7 (Table S2-2)	\checkmark	\checkmark	\checkmark	×	×	×	\checkmark
PAA ₈₆ /PPEGA ₃₃ 5/5 (Table S2-3)	\checkmark	\checkmark	×	×	×	×	\checkmark
PAA ₈₆ /PPEGA ₃₃ 7/3 (Table S2-4)	\checkmark	×	×	×	×	×	\checkmark
PAA ₈₆ /PPEGA ₃₃ 9/1 (Table S2-5)	\checkmark	×	×	×	×	×	\checkmark
$$ indicates no particle aggregation, \times indicates particle aggregation, ^a Freeze-thaw cycle proceeded at -20 °C							



Figure S1. SEM images of PMMA microspheres prepared by photoinitiated RAFT dispersion polymerization using different concentrations of PAA₈₆-DDMAT.



Figure S2. SEM images of LaF₃:Eu/PMMA composites prepared by using various carboxyl-functionalized PMMA microspheres as templates those were prepared by photoinitiated RAFT dispersion polymerization with different PAA₈₆-DDMAT/PPEGA₃₃-DDMAT weight ratios as marked in the images.



Figure S3. XRD spectra of LaF₃:Eu/PMMA composites prepared by using various carboxyl-functionalized PMMA microspheres as templates those were prepared by photoinitiated RAFT dispersion polymerization with different PAA₈₆-DDMAT/PPEGA₃₃-DDMAT weight ratios



Figure S4. SEM image of CaCO₃ crystal prepared in the absence of carboxyl-functionalized PMMA microspheres.



Figure S5. SEM images of CaCO₃ crystals prepared in the presence of various carboxylfunctionalized PMMA microspheres (prepared with different PAA₈₆-DDMAT/PPEGA₃₃-DDMAT weight ratios.

REFERENCE

[1] J. T. Lai, D. Filla and R. Shea, *Macromolecules*, 2002, 35, 6754–6756.