

SUPPORTING INFORMATION

Green synthesis of polymeric microspheres that are monodisperse and superhydrophobic via quiescent redox-initiated precipitation polymerization

Xilu Chen, Yuanyuan Ding, Dayong Ren, Zhiyong Chen*

Shandong Provincial Key Laboratory of Fluorine Chemistry and Chemical Materials, School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, China. E-mail: chm_chenzy@ujn.edu.cn

Materials

Divinylbenzene (DVB, containing 80% of 1,3- and 1,4-divinylbenzene isomers, the rest is ethylvinylbenzene or diethylbenzene) and Lauryl methacrylate (LMA, 96%) were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China) and free from inhibitor by passing through basic Al₂O₃ (Sinopharm Chemical Reagent Co. Ltd. Shanghai, China). Benzoyl peroxide (BPO) was from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Prior to use, BPO was purified by being dissolved in chloroform and subsequently precipitated after adding an equal volume of methanol. Methanol, acetic acid (AA) and chloroform were purchased from Fuyu Chemical Reagent Company (Tianjin, China). N,N-Dimethyl aniline (DMA) was obtained from Guangcheng Chemical Reagent Company (Tianjin, China).

Characterization

The particle size and size distribution of the resultant polymer particles were determined by scanning electron microscopy (SEM) using a scanning electron microscope (FEI QUANTA FEG250). All of the SEM size data indicated the averages about 150 particles each, which are calculated by the following equations:

$$D_n = \frac{\sum_{i=1}^k n_i D_i}{\sum_{i=1}^k n_i} \quad (1)$$

$$D_w = \frac{\sum_{i=1}^k n_i D_i^4}{\sum_{i=1}^k n_i D_i^3} \quad (2)$$

$$U = D_w / D_n \quad (3)$$

where U is the polydispersity index, D_n is the number-average diameter, D_w is the weight-average diameter, N is the total number of the measured particles, and D_i is the particle diameter of determined microspheres.

The structure characterization of the forming microsphere was carried out by Fourier transform infrared (FT-IR) spectroscopy. The infrared spectra of the samples in KBr discs were performed in the range of 400-4000 cm^{-1} (Spectrum one, Perkin-Elmer, USA).

Elemental analysis was performed on the Thermo Scientific FLASH 2000 CHNS/O Elemental Analyzer.

The superhydrophobic behavior was investigated by measuring the contact angle (CA) of water droplet on the surface of microsphere array using an instrument (OCA 40, Dataphysics, Germany) at room temperature (25 ± 5 °C). The microsphere array was fabricated by a simple dip-coating route. The poly(LMA-DVB) microspheres were dispersed in ethanol with a microsphere concentration of 60 mg mL^{-1} . After being ultrasonicated (200 W, 40 kHz) for 20 min, the microsphere suspension was casted on a clean surface of glass slide. The solvent was allowed to evaporate at room temperature, then the microsphere film was further dried under vacuum for 24 h prior to use.

Table S1 Preparation of poly(LMA-DVB) microspheres by quiescent redox-initiated precipitation polymerization in acetic acid under various conditions

LMA/DVB (molar ratio)	Monomer loading (vol%)	BPO (wt%)	Morphology	D _n (μm)	U	Yield (%)
50/50	20 ^a	1	Microsphere	1.41	1.121	17.6
50/50	2	1	Microsphere	0.90	1.053	1.9
50/50	5	1	Microsphere	1.66	1.034	5.4
50/50	10	1	Microsphere	2.39	1.008	12.4
50/50	15	1	Microsphere	2.77	1.016	24.0
50/50	20	1	Microsphere	3.49	1.012	29.6
50/50	30	1	Microsphere	5.64	1.127	33.8
0/100	20	1	Aggregation	n.d.	n.d.	33.8
20/80	20	1	Microsphere	3.77 ^b	1.023 ^b	35.2
40/60	20	1	Microsphere	3.50	1.019	34.0
60/40	20	1	Microsphere	3.24	1.005	31.5
80/20	20	1	Microsphere	3.11 ^b	1.017 ^b	32.3
100/0	20	1	Viscous liquid	n.d.	n.d.	n.d.
50/50	20	2	Microsphere	4.15	1.015	35.9
50/50	20	3	Microsphere	5.03 ^b	1.031 ^b	36.6
50/50	20	5	Microsphere	6.84 ^b	1.069 ^b	32.0
50/50	20	10	Aggregation	n.d.	n.d.	12.3

^a acetonitrile as the solvent; ^b not calculating irregular fragments. n.d., not determined.

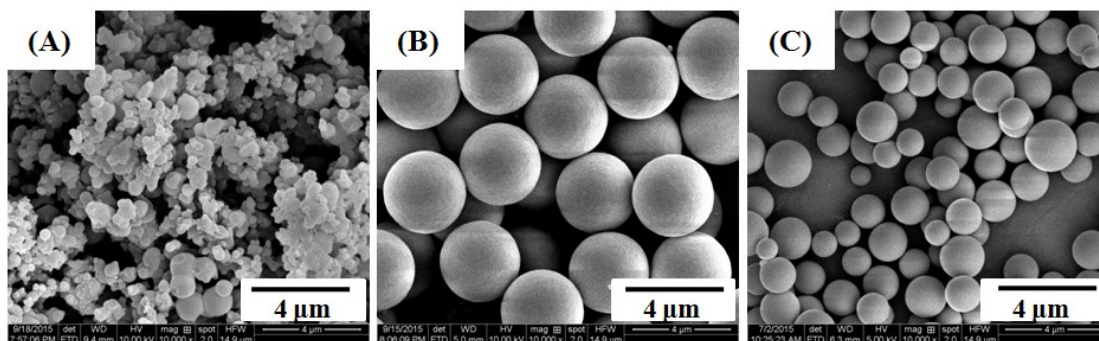


Figure S1 Poly(LMA-DVB) (50/50 molar ratio) microspheres prepared with 20 vol% monomer concentration under different stirring conditions. (A) 20 rpm min⁻¹ with acetic acid as the solvent, (B) quiescent incubation with acetic acid as the solvent, (C) quiescent incubation with acetonitrile as the solvent.

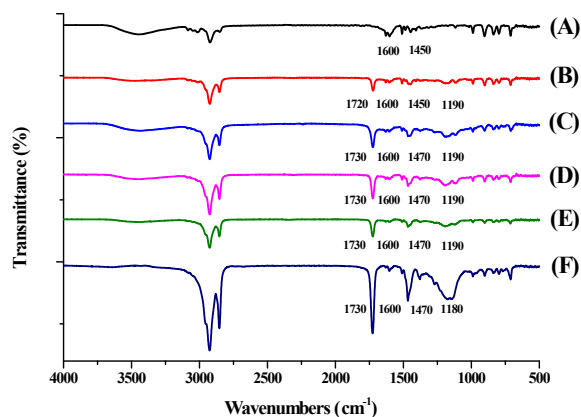


Figure S2 FT-IR spectra of poly(LMA-DVB) particles prepared with different molar ratios of LMA to DVB: (A) 0/100, (B) 20/80, (C) 40/60, (D) 50/50, (E) 60/40, (F) 80/20.

Table S2 Composition of poly(LMA-DVB) particles determined by elemental analysis

LMA/DVB (molar ratio)	Mol% of LMA		Oxygen content (wt%)	
	In feed	In copolymer	Theoretical calculation	Elemental analysis
20/80	20	15.9	4.13	3.39
40/60	40	27.7	7.12	5.39
50/50	50	36.5	8.32	6.66
60/40	60	39.7	9.38	7.08
80/20	80	64.1	11.15	9.78

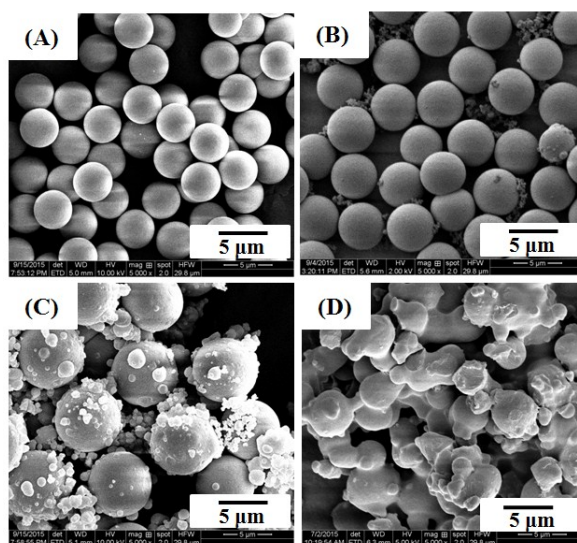


Figure S3 SEM images of poly(LMA-DVB) particles prepared at different initiator concentrations. (A) 2 wt%, (B) 3 wt%, (C) 5 wt%, (D) 10 wt%.

Table S3 Solubility parameters of acetonitrile, acetic acid, LMA and DVB and their corresponding densities

Reagent	δ^a (MPa ^{1/2})	δ_d (MPa ^{1/2})	δ_p (MPa ^{1/2})	δ_h (MPa ^{1/2})	Density (g mL ⁻¹ , 20 °C)
Acetonitrile	24.4	15.3	18.0	6.1	0.786 ^b
Acetic acid	21.4	14.5	8.0	13.5	1.051 ^b
LMA	15.4	14.4	2.2	5.1	0.866 ^b
DVB	17.4	17.4	0.8	0	0.910 ^c

^a $\delta = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2}$, δ_d , δ_p , and δ_h from ref¹; ^b from ref²; ^c from database of Aladdin Chemistry Co. Ltd.

References

- 1 C. M. Hansen, *Hansen Solubility Parameters: A User's Handbook*, 2nd ed., CRC Press, Boca Raton, 2007.
- 2 W. M. Haynes, *CRC Handbook of Chemistry and Physics*, 95th ed., CRC Press, Boca Raton, 2014.