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Superwettable Porous Spheres Prepared by Recyclable Pickering Emulsion Polymerization for Multifarious Oil/Water Separation

Chao Wang^{a,b}, Hui Chi^a, Fan Zhang^{a,b}, Xinyue Wang^{a,b}, YinChuan Wang^a, Hao Zhang^a, Yungang Bai^{a,b}, Ying Tan^{c,*}, Kun Xu^{a,*} Pixin Wang^{a,b}

^a Key Laboratory of Polymer Ecomaterials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China

^b University of Science and Technology of China, Hefei 230026, PR China

^c Wenzhou Institute, University of Chinese Academy of Sciences, Wenzhou 325001, PR China

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EXPERIMENTAL

Materials. Acidified wax corn starch (Mv = 200000) was obtained according to a previously reported method. Butyl glycidyl ether (BGE) was purchased from Tokyo Chemical Industries (Tokyo, Japan). Trimethylolpropane triacrylate (TMPTA), 2,2-Dimethoxy-2-phenylacetophenone (DMPA) were bought from Ailan Chemical Technology Co., Ltd. (3A Chemical) (Shanghai, China). Surfactants Span 80 and Tween 20, toluene, 1,2-dichloroethane, naphtha, white oil were supplied by Xilong Scientific Co., Ltd. (Shantou, China). Deionized water was utilized throughout the study.

Synthesis of 2-hydroxy-3-butoxypropyl starches (HBPS) and fluorescein labelled HBPS. To obtain HBPS with different degrees of substitution, the following experiments were carried out. Firstly, 8.1 g of obtained acidified wax corn starches were dispersed in 20 mL of deionized water and heated to 75 °C. Secondly, 20 mL of sodium hydroxide solution (including 1g NaOH) was added to starch dispersion and stirred for one hour, followed by a certain amount of BGE (according to degrees of substitution), and reacted at 75°C for 5 hours. After the reaction, the dispersion was cooled in an ice bath and neutralized with hydrochloric acid. Then, the supernatant was inverted and an appropriate amount of tetrahydrofuran was added for ultrasonic dissolution, and the obtained solution was dropped into a large amount of water for precipitation. This process was repeated three times. Finally, the precipitate was dried in a freeze-dryer and sealed for storage. Reference to our previous work, the degree of substitution (DS) of HBPS was determined by ¹H NMR spectra. according to Equation 1:

$$DS = \frac{B/3}{A/4} = 1.33\frac{B}{A}$$
 (1)

where A was the integral of the peaks representing the hydroxyl and H-1 protons at 4.5–6.6 ppm and B was the integral of the area of methyl protons represented at 0.8 ppm.

The method of synthesizing fluorescein labelled HBPS was as follows: 1.0 g of HBPS was dissolved in 10 mL of DMSO and reacted with 25 mg of FITC in the presence of 0.1 mL of DBTDL for 5 h at 100 °C. Then, the FITC labelled HBPS was precipitated with water and purified by dialysis in deionized water until the filtrate was not fluorescent.

Preparation of HBPS particles. HBPS particles were prepared by nano-coprecipitation. Typically, 2 g of HBPS obtained by the above method was dissolved in 400 mL tetrahydrofuran, and then the resulted solution was dropped into 400 mL deionized water with a drop funnel. Finally, stirred continuously at room temperature until all tetrahydrofuran volatilized, and the final solution was the HBPS particles dispersion.

Preparation of Pickering emulsions stabilized by HBPS particles. In this experiment, the composition of the Pickering emulsion with an oil-water ratio of 1:2 was toluene as the oil phase and HBPS particle dispersion as the aqueous phase. The specific procedure is as follows: 5 mL of toluene and 10 mL of 0.5% HBPS particle aqueous dispersion were poured into a 20 mL reagent bottle and leaved in water bath with a certain temperature for 30 minutes. Then the starch-based Pickering emulsion was obtained by homogenization with an IKA Ultra Turrax T18 homogenizer operating at 15,000 rpm for 120 s.

Preparation of microspheres by recyclable polymerization. Firstly, 2 g of monomer (TMPTA) and 0.02 g of photoinitiator (DMPA) were dissolved in 20 mL toluene by ultrasound, followed by addition of 40 ml 0.5% HBPS-4 particle dispersion and stored in an ice bath for 30 minutes. The

homogenizer was then used to mechanically shear for 120 seconds at 15,000 rpm, and bubbled with nitrogen gas for five minutes before sealing with plastic wrap. Secondly, the prepared emulsion was photopolymerized under a UV radiator apparatus for 30 minutes in an ice bath. Next, the resulted emulsion was placed in a 35°C water bath until it was demulsified and then filtrated with a vacuum pump. Finally, the collected polymer microspheres were washed three times with anhydrous ethanol, dispersed in water, and then freeze-dried. On the other side, the collected filtrate is separated by a separator funnel, and the obtained water phase was directly used for the next polymerization.

Separation of emulsion. The polymer microspheres obtained by photopolymerized in above were used for emulsion separation, and the separation of emulsions was conducted in a syringe barrel. Specifically, surfactant Tween 20, oil and water were mixed at a volume ratio of 10:10:100, and dispersed by a homogenizer at 15000 RPM for 2 minutes to form a stable oil-in-water emulsion. For the preparation of stabilized water-in-oil emulsions, Span 80, water and oil were homogenized in the same proportion. By the way, naphtha, white oil, soybean oil and 1,2-dichloroethane were selected to prepare the emulsion in this experiment. Then, about 0.1g polymer particles were put into the syringe barrel, followed by adding a certain amount of emulsion as the feed for each separation, and the corresponding filtrate was collected for the measurement of oil or water content. It should be noted that the emulsion separation was performed at a pressure of -0.5 bar provided by a vacuum pump. The separation efficiency R (%) was calculated by measuring the residual oil or water concentration of the filtrate using gas chromatography (for oil-in-water emulsion) and Karl-Fischer moisture meter (for water-in-oil emulsion) respectively, according to Equation 2:

$$R(\%) = \frac{C_e - C}{C_e} \times 100\%$$
(2)

where C_e and C are the concentrations of oil or water in the feed emulsions and the collected filtrate, respectively. The flux refers to the volume of the collected filtrate (water or oil, according to the type of feed emulsions) within a certain period of time and pressure.

Characterization. The ¹H NMR spectra of HBPS samples was measured on a Bruker AV400 spectrometer (400 MHz, Ettlingen, Germany) and recorded in d6-DMSO at 600M and 25 °C. The size of HBPS particles with various DS present in aqueous dispersions at 25 °C were measured by dynamic light scattering (DLS) using a 90 Plus particle size analyzer (PSA; Brookhaven) with dilute suspensions (concentration approximately 0.01% in distilled water). The sample suspensions were dropped on a silica surface at a certain temperature and freeze-dry after soaking in liquid nitrogen to obtain the microscopic appearance of the HBPS nanoparticles by scanning electron microscopy (SEM) using a Merlin FE-SEM (ZEISS). For transmission electron microscope (TEM) characterization, a dispersion of polymer spheres was dropped on the copper grids and dried at room temperature. The transmittance of HBPS particles in aqueous suspensions (0.5%, w/w) was measured with a UV-vis spectrophotometer (PerkinElmer Lambda 35, America) at 500 nm under a heating rate of 2 °C/min. The dynamic interfacial tension of the HBPS-4 at the n-hexane-water interface was measured using the pendant drop method (Krüss DSA100) with a constant drop volume of 10 μ L using a computer-driven dosing system. N₂ adsorption/desorption isotherm of polymer spheres was measured by Autosorb-iQ analyzer (Quantachrome Instruments, American) and the specific surface areas and total pore volumes were obtained employing Brunauer-Emmett-Teller (BET) method. The morphology of the emulsion droplets and polymer spheres were observed with digital optical microscopy (Nikon K550L, Japan), and the image was processed by microscopic analysis software (Image J) to obtain the size of the droplets and spheres. The contact angles on the surface of the polymer spheres were measured by a contact angle measuring instrument (Krüss, DSA100).

TABLES AND FIGURES

		Area of protons(S)		_				
Sample	BGE:AGU ^a	5.8-4.4 ppm (OH-2,3,6,8;H-1) ^b	1.55-1.25 ppm (H-11,12)	0.87 ppm (H-13)	DS^c	Size(nm) ^d	LCST(°C)	Contact angel(°) ^e
HBPS-1	0.50	1.00	0.36	0.26	0.35	59.19		56.1
HBPS-2	0.75	1.00	0.49	0.36	0.48	62.12	36.0	61.9
HBPS-3	1.00	1.00	0.75	0.57	0.76	80.50	17.8	84.5
HBPS-4	1.25	1.00	0.87	0.65	0.87	97.48	13.0	95.1
HBPS-5	1.50	1.00	0.91	0.68	0.91	124.25	12.0	96.4
HBPS-6	1.75	1.00	1.12	0.83	1.11	149.90	4.5	101.4
HBPS-7	2.00	1.00	1.32	0.98	1.31	216.23		104.9

Table S1 Characterization of HBPS particles

^{*a*} Molar ratio.

^{*b*} Area of OH-2,3,6,8 and H-1 protons was set as the basic value 1.

^{*c*} Degree of butyl glycidyl ether substitution determined by ¹H NMR.

^{*d*} Determined by DLS at 25 °C.

^{*e*} Determined at 25 °C.

	Mean diameters (µm)							
	1 st cycle	2 nd cycle	3rd cycle	4 th cycle	5 th cycle			
Emulsions	18.06	17.22	8.99	11.80	13.96			
Polymer spheres	10.22	13.19	10.52	11.45	11.57			

Table S2. Size of emulsion droplets and polymer spheres at each cycle polymerization.



Figure S1. FT-IR spectra of HBPS with different additive amount of BGE.



Figure S2. ¹H NMR spectra of HBPS, where R = H or substituent (depending on the DS).



Figure S3. The water contact angel of HBPS with different DS.



Figure S4. (a1-g1) Transmittance changes for 0.5% (w/v) aqueous solutions of HBPS with different DS as obtained by UV–vis spectrophotometry at 500 nm with a heating rate of 1.0 °C/min. (a2-g2) Emulsification and demulsification of emulsions stabilized by HBPS. (h) Reversible process of emulsification/demulsification.



Figure S5. The emulsion stability index (ESI) of emulsions stabilized by 0.5 wt% HBPS-4 at different temperature.



Figure S6. SEM images of poly TMPTA by a simple solution polymerization with 0.2 w/v% monomers. (a) Primary products. (b) Products of double concentration. (c) Products of eight times concentration. The white bar corresponded to 2 μ m.



Figure S7. Separation efficiency and separation flux of polymer spheres at initial time and after 24 hours of continuous separation processes: (a) water-in-oil emulsion separation, (b) oil-in-water emulsion separation. The oil phase of the emulsion used in this test is toluene.