Supporting Information

Nanohybrids from direct chemical self-assembly of poly(styrene-*alt*-maleic anhydride) as pH-responsive particulate emulsifiers

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1. Synthesis of SMA-PAPTES nanohybrids

1.1 Materials and Characterization

Styrene (St, Sinopharm Chemical Reagent Co., Ltd., SCRC) was distilled under reduced pressure and then stored at 5 °C prior to use. Maleic anhydride (MAn, analytical grade, Sigma-Aldrich) was used as received. 2, 2-Azobis (isobutyronitrile) (AIBN, AR, SCRC) was recrystallized twice from methanol before use. All water was first deionized by reverse osmosis and purified to a resistivity of 18.2 MΩ·cm using a Millipore water purification system.

^{1}H NMR spectra were recorded on a Bruker DMX500MHz spectrometer using tetramethylsilane as an internal standard. The molecular weight and molecular weight distribution index of the copolymers were determined using gel permeation chromatography (GPC,HP1100) with DMF as a mobile phase at a flow rate of 1.0 mL·min^{-1} at 35 °C. Polystyrene standards were used for the calibration of molecular weight. FTIR spectra were carried out on FTLA 2000 spectrometer.

1.2 Synthesis of poly(styrene-*alt*-maleic anhydride)

Alternating copolymers poly(styrene-*alt*-maleic anhydride) (SMA) were synthesized through the free radical copolymerization of electron-donating monomers of styrene (St) and electron-accepting monomer maleic anhydride (MAn) using AIBN as an initiator. St and MAn were dissolved in toluene at molar ratios of 5:6 and AIBN, 0.3% of the total molar weight of monomers, was added into a 250 mL one-necked round-bottom flask. The mixture was degassed with N2 gas for 30 min and sealed under vacuum. After 30 min of stirring at room temperature, the ampoule was placed in a preheated oil bath (65 °C) for 20 h under

stirring. The resultant copolymers were purified by reprecipitation three times into hot toluene and then were dried under vacuum at 80 °C for 24 h (yield: 90 %).

GPC: Mn = 161kg/mol, Mw = 185 kg/mol, PDI=1.54, PS as standard and DMF as eluent solvent. 1H NMR (DMSO-d6): Molar ratio of styrene unit to maleic anhydride units is 1.01：1, determined by 1H NMR. Hence, the obtained SMA could be used as strictly alternating copolymer.

1.4 FTIR characterization

The FT-IR spectras of SMA, pre-SMA-PAPTES nanohybrids and SMA-PAPTES nanohybrids were shown in Figure S1.The FT-IR spectra for pure SMA and pre-SMA-PAPTES nanohybrids (without reflux) are shown in Figure S1 (a and b). Compared with Figure 2a, some new bands appear in Figure 1b. The peak at 1712 cm^{-1} ascribes to the acid C=O stretching, and the peaks at 1635 cm^{-1} and 1570 cm^{-1} are associated with amide C=O stretching and N-H bending mode absorptions respectively. Moreover, the appearance of peaks at 1079 cm^{-1} and 957 cm^{-1} are assigned to Si-O-C and Si-OH stretching mode. These changes confirm that the imidization reaction between SMA and APTES occurs in the pre-reaction, including the partial hydrolysis of siloxane groups due to the presence of trace amount of water in the acetone.

The SMA-PAPTES nanohybrid aqueous disperation was freeze-dried and the dry sample was analyzed as KBr pellets by FT-IR (Figure S1c). The broad peak from 1000 to 1119 cm^{-1} results primarily from the absorption due to Si-O-Si stretching, which suggests the polycondensation of the APTES. What's more, the broad envelope stretching from 3700 to 3000 cm^{-1} is attributed to the hydrogen bonding interactions between OH groups. Combined

with the band of C=O stretching, indicating that there are carboxyl groups in nanohybrids. The carboxyl groups were generated by ring-open of maleic anhydride (MAn) induced by amidation reaction and hydrolysis in basic solution.
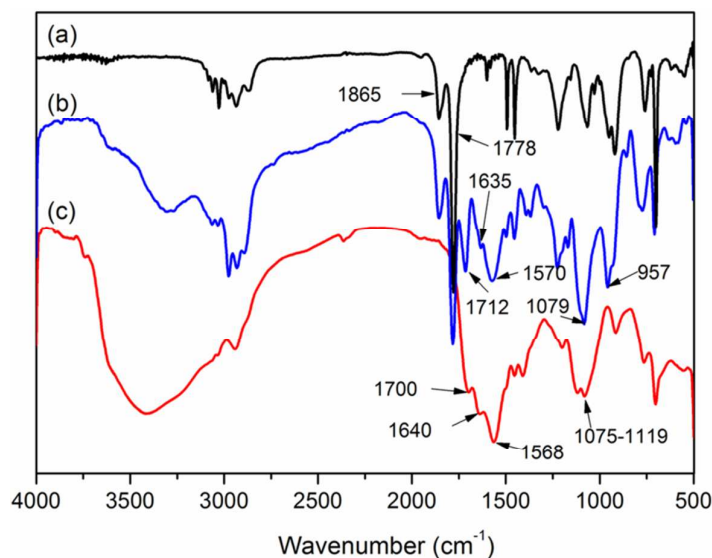

Figure S1. FT-IR of SMA (a), pre-SMA-PAPTES nanohybrids (without reflux time) (b) and SMA-PAPTES nanohybrids (c).

Table S1. Assignments of the Main Infrared Absorption Bands (cm^{-1})

for FT-IR spectra of (a), (b) and (c)

| band position/cm^{-1}	assignment
(a) 1865, 1778	ν C=O (anhydride)
(b) 1712, 1635, 1570, 1079, 957	ν C=O (acid), ν C=O (amide), δ N-H, ν Si-O-C, ν Si-OH
(c) 3700-3000, 1700, 1640, 1568, 1000-1119	ν (OH····O), ν C=O (acid), ν C=O (amide), δ N-H, ν Si-O-Si

The FT-IR results are summarized in Table S1. Taken together, these results indicate that SMA and APTES undergo aminolysis and hydrolysis in pre-reaction and the SMA-PAPTES nanohybrids are obtained via self-assembly of SMA induced by in-situ polycondensation.
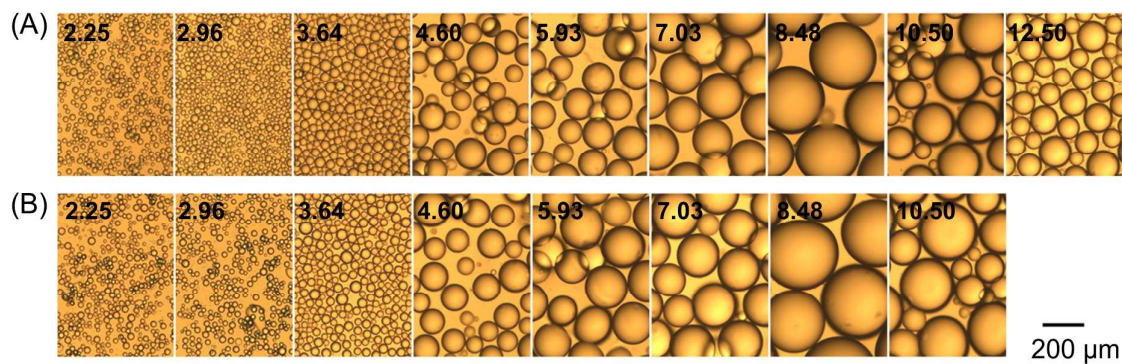
2. The emulsifying performance of SMA-PAPTES nanohubrids
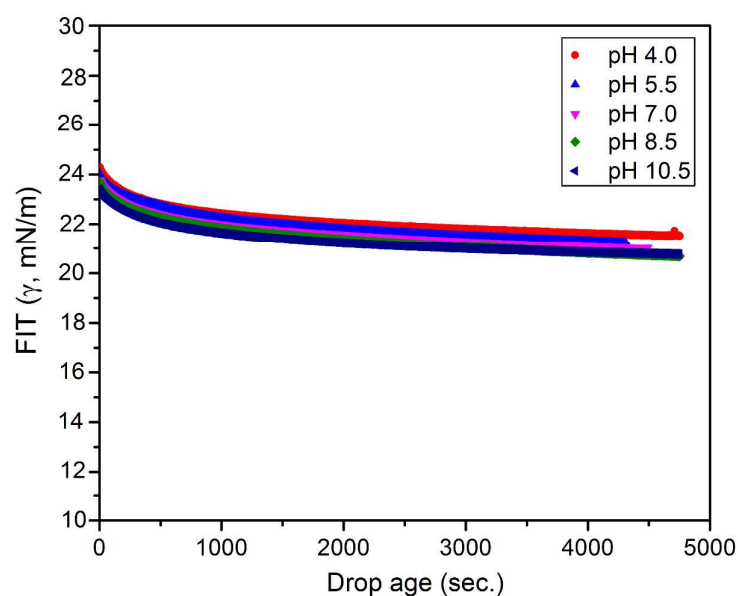

Figure S2. Time-dependent IFT curves for paraffin oil against PBS-burffer with different pHs without nanohybrids.
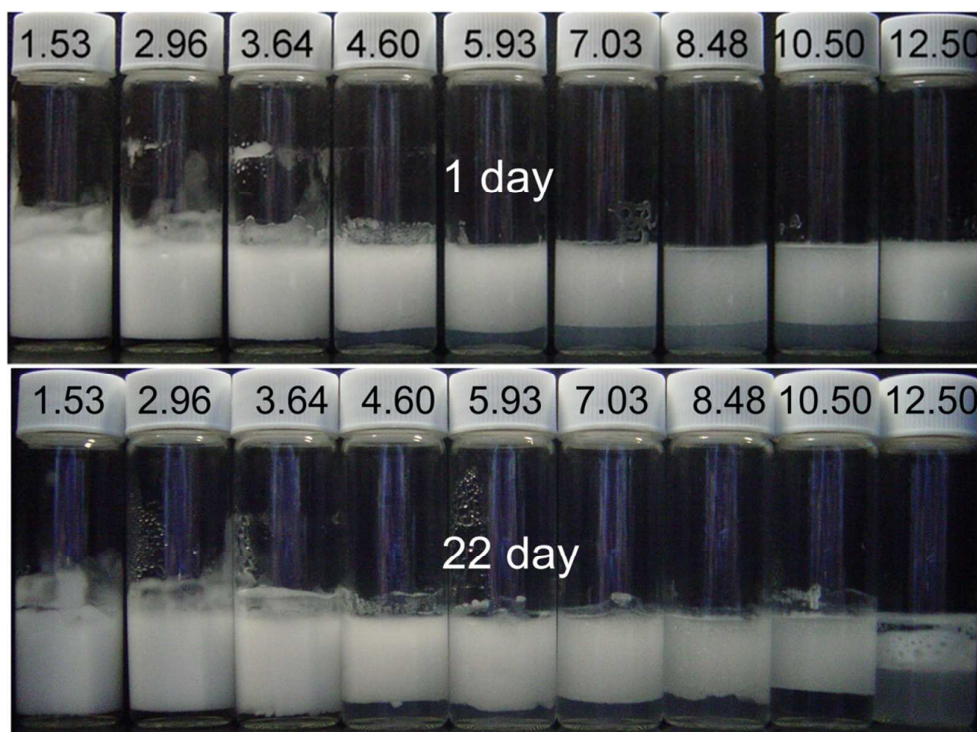
Figure S3. Digital pictures of paraffin oil-*in*-water emulsions stabilized by SMA-PAPTES nanohybrids at various pH values. The concentration of the nanohybrids is 2 mg·mL^{-1}.

Figure S4. Optical images of paraffin oil-in-water at various pHs stabilized by 2 mg·mL^{-1} HSMASi-0.5 nanohybrids   with placement durations for 1 day (A) and 22 days (B).
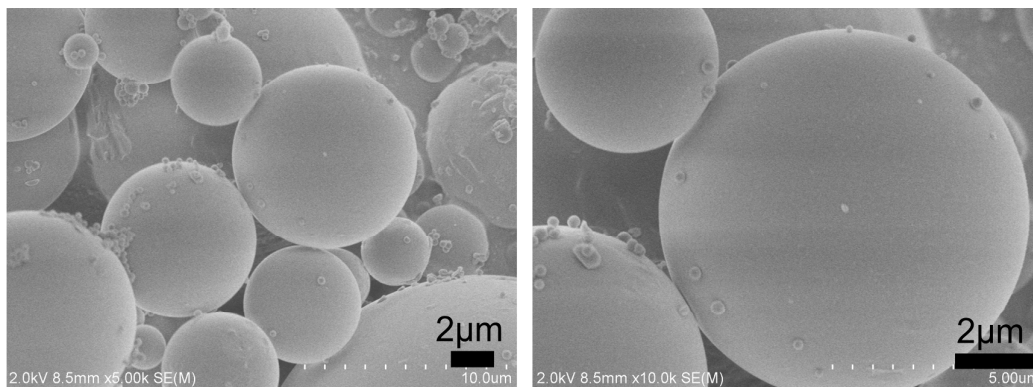
Figure S5. SEM images of the solid polystyrene droplets stabilized by HSMA at different

magnifications.