Electronic Supplementary Material (ESI) for Soft Matter.


# Supplementary Information

## Liquid marbles prepared from pH-responsive self-assembled micelles

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# 1. Synthesis of poly(styrene-*co*-acrylic acid-*co*-2,2,3,4,4,4-Hexafluorobutyl methacrylate)

## 1.1 Materials and Characterization

Styrene (St) and acrylic acid (AA) (Sinopharm Chemical Reagent Co., Ltd. SCRC) were purified by vacuum distillation prior to use. 2,2,3,4,4,4-Hexafluorobutyl methacrylate (HFMA) and Rhodamine B were supplied by J&K Scientific Ltd.. α',α'-Azobis-[isobutyronitrile] (AIBN) (SCRC) was recrystallized twice from methanol before use. Dioxane, petroleum ether (30~60°C), *N,N*-dimethylformamide (DMF) and tetrahydrofuran (THF) (AnalaR, SCRC) were used without further purification.

$^1$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 PSAF

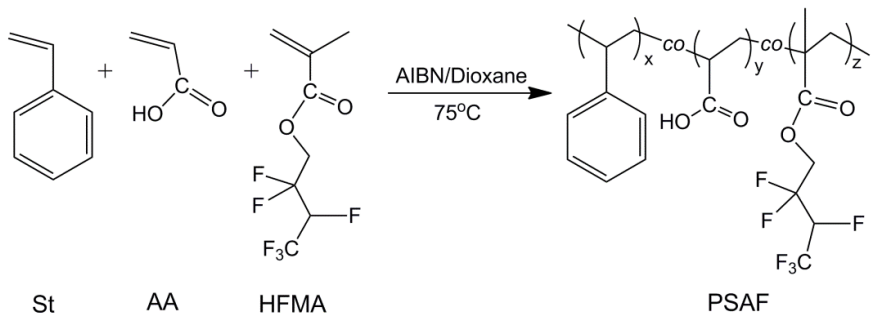


**Fig. S1** Synthetic route for PSAF.

Random copolymers poly(styrene-*co*-acrylic acid-*co*-2,2,3,4,4,4-Hexafluorobutyl methacrylate) (PSAF) were synthesized through the free radical copolymerization. St AA, and HFMA were dissolved in dioxane at molar ratios of 1:1:1 and AIBN, 2% of the total molar weight of monomers, was added into a 250 mL one-necked round-bottom flask. The mixture was degassed with $N_2$ 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 24 h under stirring. The resultant copolymers were precipitated by adding the solution into an access amount of petroleum ether. The precipitation was dissolved in THF, and then precipitated by petroleum ether. For purifying the resultant, the step described above was repeated for three times. The resultant was dried under vacuum at 35 °C for 24 h.

GPC: $M$n=1.21×10$^4$，$M$w=2.35×10$^4$，$M$w/$M$n=1.94. PS as standard and DMF as eluent solvent. $^1$H NMR (DMSO-*d6*): Molar ratio of monomer units was determined by $^1$H NMR, $n$(St) : $n$(AA) : $n$(HFMA) = 1.00 : 0.69 : 0.96.

**1.3 FTIR characterization**

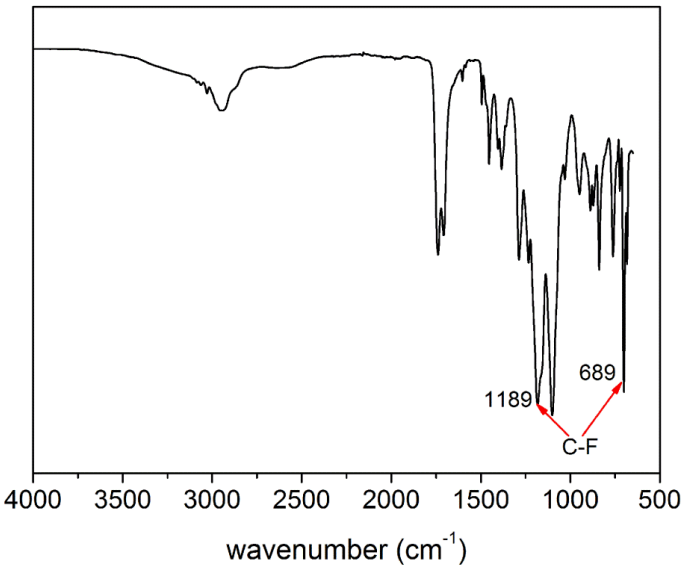

**Fig. S2** FT-IR spectrum of PSAF.

## 2. Self-assembly of PSAF

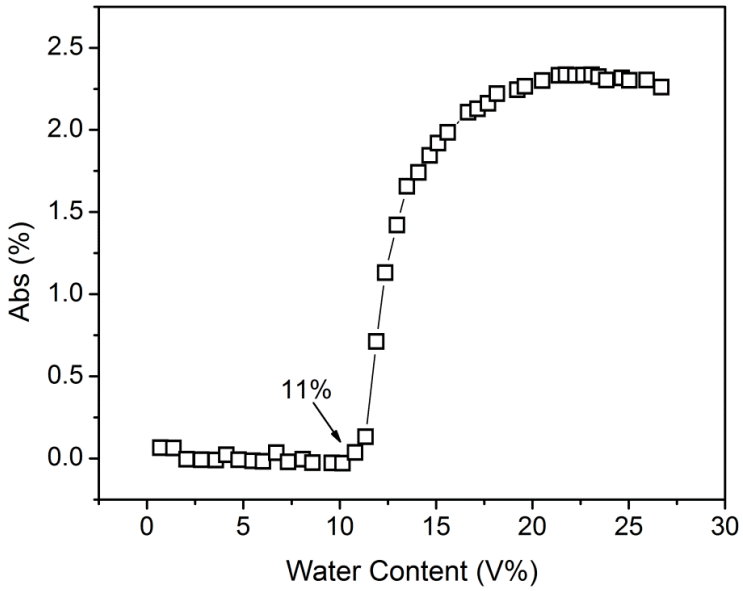


**Fig. S3** Turbidity change of PSAF solution in DMF with water content.

## 3. Characterization of liquid marbles

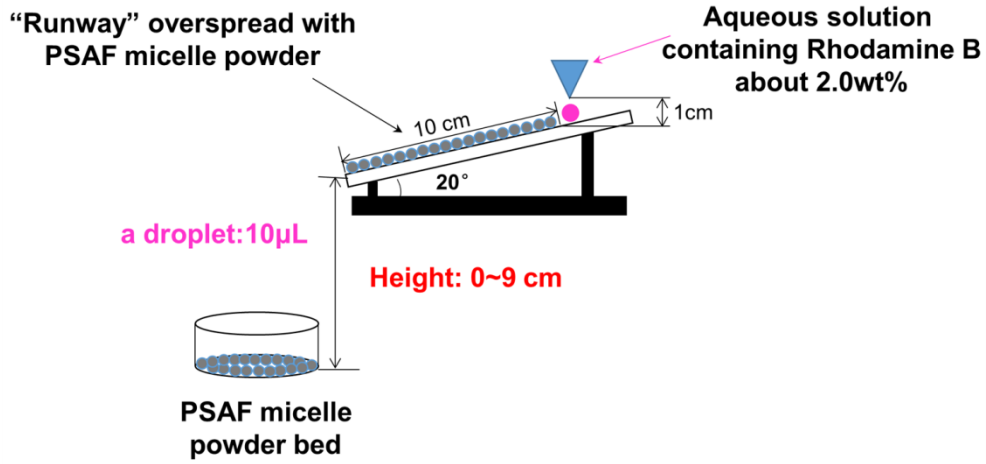


**Fig. S4** Illustration of home-made droplet roller apparatus.