Supplementary Information

Superhydrophilic fluorinated polyarylate membranes via *in situ* photocopolymerization and microphase separation for efficient separation of oil-in-water emulsion

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Experimental section

Materials

Bisphenol AF, Terephthaloyl chloride (TPC), Isophthaloyl chloride(IPC), and Benzyltriethylammonium chloride (BTEAC) were obtained from Sinopharm Chemical Reagent Co., Ltd. Sodium acrylate, n-butyl acetate (BA), Tri(ethylene glycol) diacrylate (TEGDA), 2,2-Dimethoxy-2-phenylacetophenone (DMPA) were supplied by Sigma-Aldrich. General other chemicals such as tetrahydrofuran(THF), toluene, hexadecane, sodium dodecyl sulfate(SDS) in reagent grade were used as received from Kemiou Chemical Co., Tianjin, China.

Fabrication of the SFPAR and FPAR membranes

According to our previous report method[1], a FPAR was prepared by interfacial

polymerization (Fig. S1a). The number-average molecular weight of the obtained PAR is 93,000 and the polydispersity index is 1.76 (Fig. S2). After the complete dissolution of 6.35 g FPAR, 0.95 g sodium acrylate, 2.6 g BA, 0.08 g TEGDA, 0.02 g DMPA in 87 g THF at room temperature under nitrogen atmosphere (Fig. S1b), the formed solution was placed in a nitrogen blanket and poured into glass mold made of two pre-cleaned glass plates with 2.5 mm spacing separated by rubber. *In situ* photocopolymerization was then carried out by irradiation using UV light (365nm, 30w UV lamp) for 4 h. Subsequently, the resultant solution layer with the lower glass plate of the mold were immediately immersed into 25 °C the mixture of water and THF (8:2, v/v) as a coagulation bath. After solidification, the membrane was transferred to 40 °C pure water for 48 hours to remove the residual solvent and unreacted monomer and the forming SFPAR membrane was natural dried at room temperature**.** In addition, using the above method, FPAR membranes without acrylate copolymer was also fabricated for comparison.

Preparation of oil-in-water emulsions

Three kinds of oil-in-water emulsions were prepared by adding surfactant and oil into water under vigorous stirring[2]. In brief, for toluene-in-water emulsion, 0.1 g SDS was added into 1mL toluene, and then 70 mL water was also added. The mixture was vigorously stirred for 3 h. For hexadecane-in-water emulsion, hexadecane (1mL), water (90 mL) and SDS (0.015 g) were mixed, and then stirred for 5 h. soybean oil-in-water emulsion was prepared by mixing soybean oil (1.5 g) and water (90 mL) with addition of SDS (0.03 g) under vigorous stirring. The obtained emulsions are stable

overnight without precipitation. The droplet sizes were in the range of several hundreds nanometer to ~10 μm.

Characterization

ATR-FTIR characterization of the membranes was performed using a Bio-Rad FTS-135 spectrometer in the scan range of 4000-500 cm^{-1}. A scanning electron microscope (SEM, FEL Nova Nano 430) was utilized to investigate the morphologies of the membranes and a Nano Measurer 1.2 was utilized to calculate both pore size and pore distribution around the surface of SFPAR membrane. The surface composition was measured by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000C ECSA) using at a 90 ° take-off angle. Contact angles were measured with an optical contact angle meter system (Data-physics OCA40, Germany), and the measurements were carried out with 8 μL water droplet. The molar mass distribution was determined in a Waters 1515 gel permeation chromatography (GPC) with THF as the eluent flowing at 1 mL/min. The tensile strength of membranes (sized at 5 cm ×1 cm) was determined using a universal testing machine (5560, Instron, US).

Emulsion Separation Experiments: Emulsion separation experiments were carried out with a vacuum driven filtration system at 0.07 MPa (vacuum degree -0.07 MPa) on the basis of the reported method[3]. The as-prepared membrane was fixed between two glass tube with a metal clamp and a certain amount of oil-in-water emulsion were poured onto the upper glass tube. The flux was determined by calculating the permeated volume of an emulsion within a certain time. DLS measurement was performed on a Zetasizer Nano ZS (Malvern, UK). The oil content in water was

measured by a total organic carbon analyzer (TOC-LCSH, Shimadzu).

Result

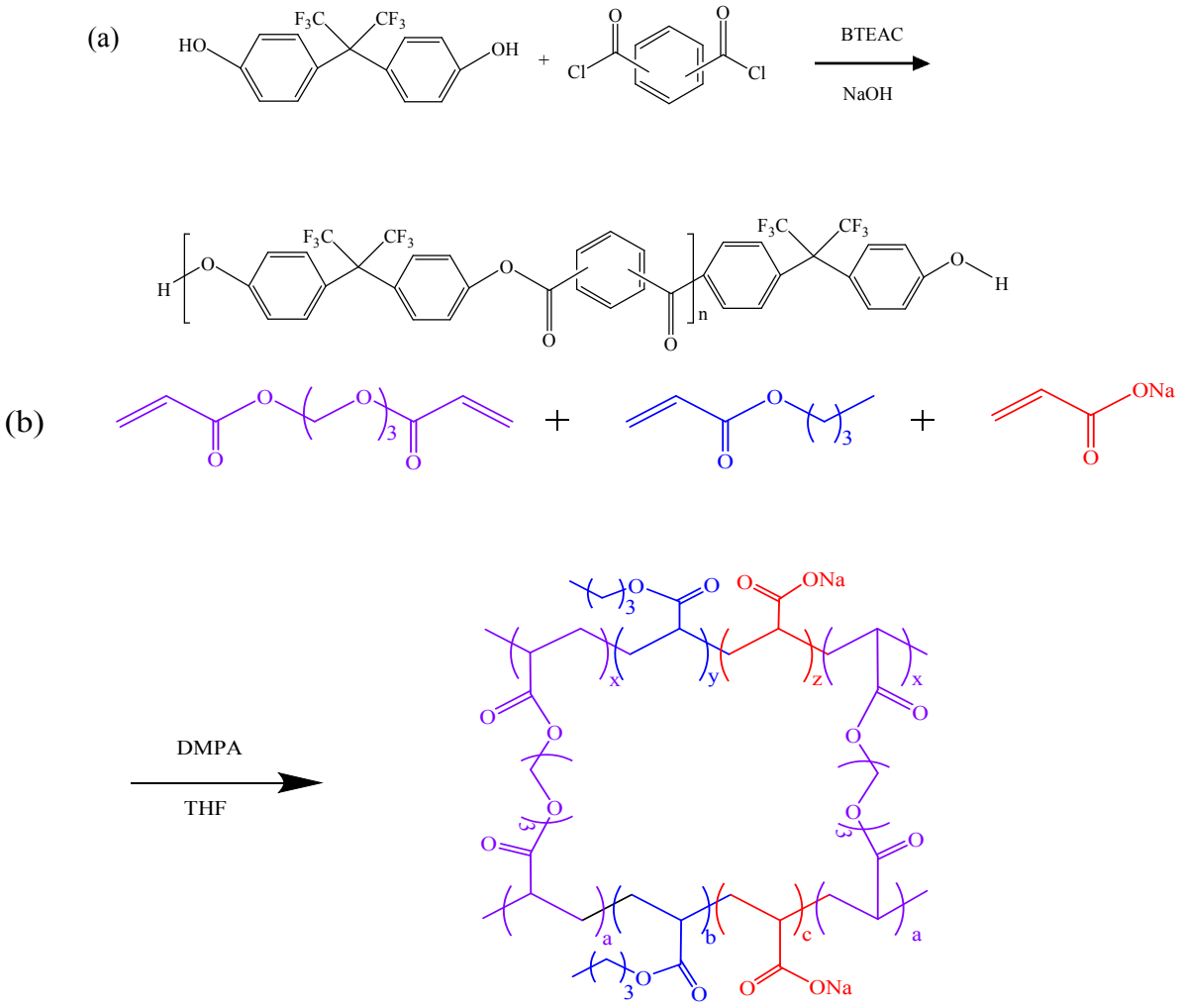

Fig. S1 Synthetic route of FPAR (a) and P(BA-co-AANa) (b).

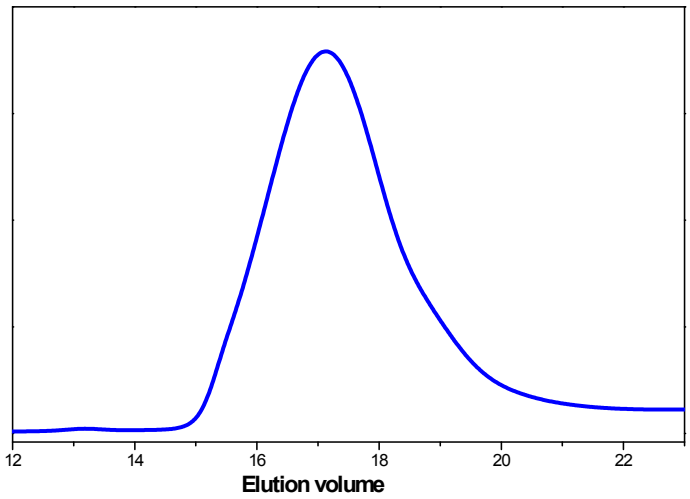

Fig. S2 GPC curves of FPAR. The number-average molecular weight of FPAR is 93,000 and the polydispersity index is 1.76.

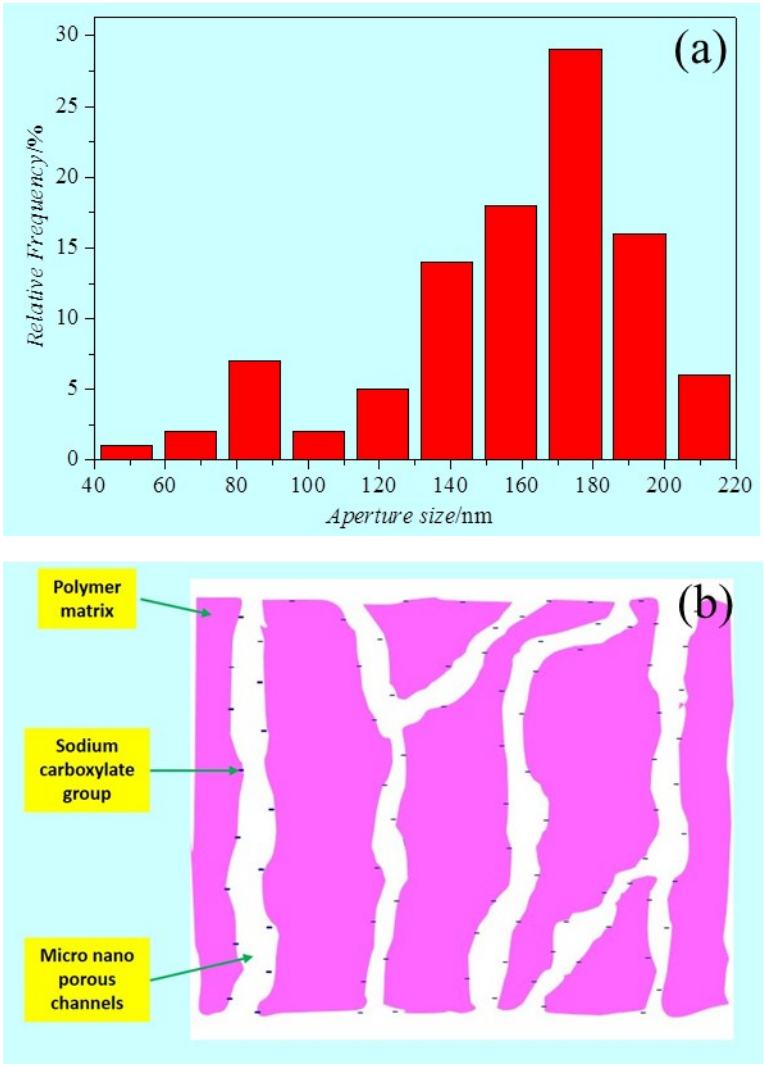

Fig. S3 The pore size distribution histogram (a) and diagram with porous structure (b) of the

SFPAR membrane

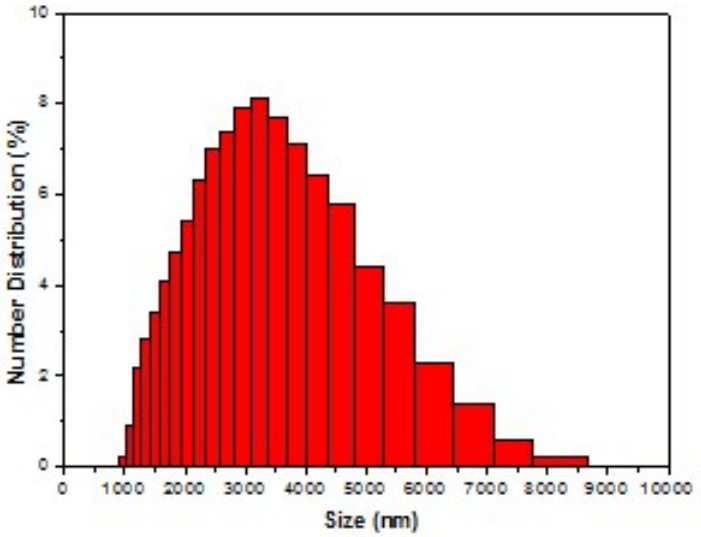

Fig. S4 Droplet size distribution of the toluene-in-water emulsion by the dynamic light scattering (DLS)

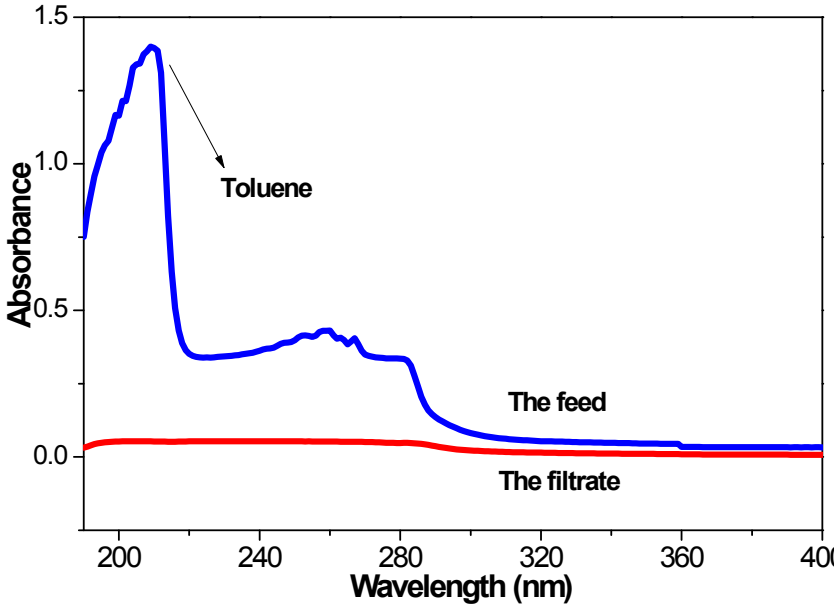

Fig. S5 UV-VIS spectra for the toluene-in-water emulsion before and after filtration. No characteristic peak for oil was observed in the spectrum of the filtrate.

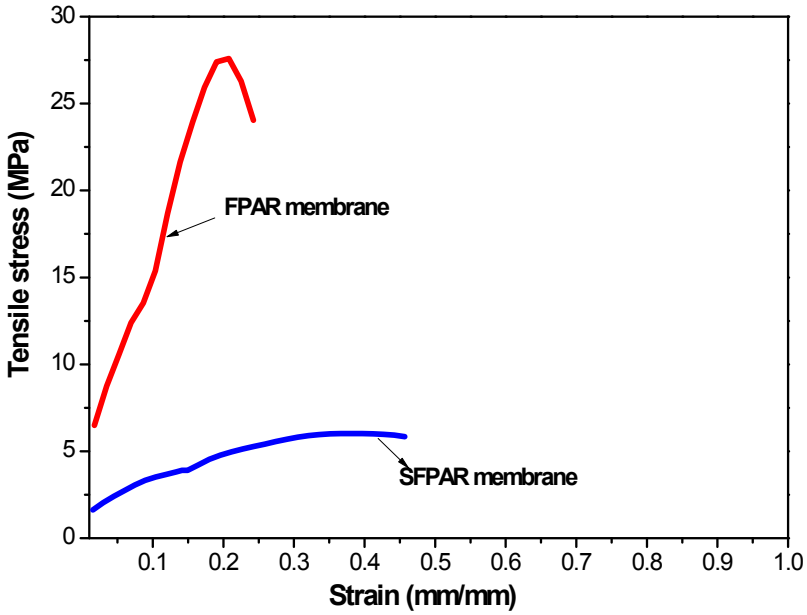

Fig. S6 Stress-strain curve of the FPAR and SFPAR membranes (sized at 5cm × 1 cm)

Tab. S1 Oil purity of the filtrate separated from the oil-in-water emulsions

Emulsion	Oil purity of the filtrate (ppm)
toluene-in-water	54±17
hexadecane-in-water	73±9
soybean oil-in-water	61±14

References

1. H. Li, X. Zhao, P. Wu, S. Zhang, B. Geng, *J. Mater. Sci.*, 2016, **51,** 3211–3218.
2. M. Tao, L. Xue, F. Liu, L. Jiang, *Adv. Mater.*, 2014, **26,** 2943-2948.
3. C. Gao, Z. Sun, K. Li, Y. Chen, Y. Cao, S. Zhang, L. Feng, *Energy Environ. Sci.*, 2013, **6**, 1147-1151.