

## **Electronic Supplementary Information (ESI)**

### **High internal phase emulsion (HIPE) organogels from charge-driven assembled polymer organogels**

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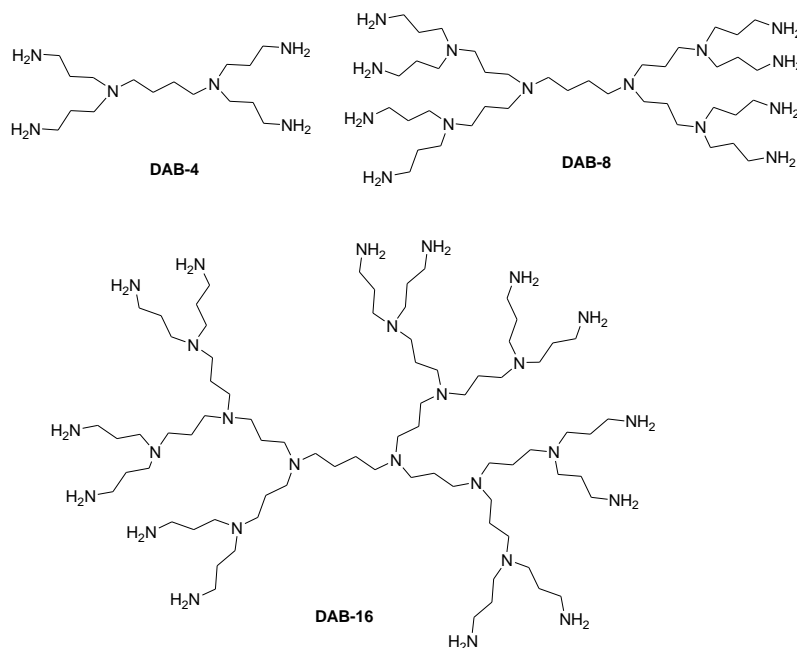
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#### **Table of Contents**

<b>1. Experimental section.....</b>	<b>2</b>
<b>2. Ionic interaction between SSEBS and PPI dendrimers.....</b>	<b>3</b>
<b>3. Responsiveness of organogels .....</b>	<b>4</b>
<b>4. Movies.....</b>	<b>5</b>
<b>5. References.....</b>	<b>5</b>

## 1. Experimental section

**Materials.** Polypropylenimine (PPI) dendrimers were purchased from Sigma-Aldrich, and generation 1 (DAB-4), generation 2 (DAB-8) and generation 3 (DAB-16) of PPI dendrimers were used (Fig. S1). Deionized water was used in all experiments. Triblock ionomer, namely sulfonated polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene (SSEBS), was prepared from polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene (SEBS) according to the method described in our previous study,<sup>1</sup> and it had 17.95 mol % of polystyrene on SEBS grafted with -SO<sub>3</sub>H groups by titration.



**Fig. S1** Chemical structures of PPI dendrimers DAB-4, DAB-8 and DAB-16.

**Preparation of organogels.** The procedure for the preparation of organogels was similar to that described in our previous paper.<sup>1</sup> In brief, 5 % (w/v) SSEBS was obtained by dissolving SSEBS into mixed solvents of toluene and methanol (98/2, v/v), and then the solution was neutralized with 2 % (w/v) PPI dendrimers of toluene solution. After addition of PPI dendrimer solution into SSEBS solution, the mixture was stirred acutely. All the organogels were prepared at stoichiometric ratio with  $[-\text{SO}_3\text{H}]/[\text{NH}_2+\text{N}] = 1$  by addition of different amounts of PPI dendrimer solutions into 1 mL of SSEBS solutions.

**Preparation of HIPE gels.** HIPE organogels were prepared by shearing a mixture of salt aqueous solutions (4.5 mL) with different NaCl concentrations, THF (1 mL) and organogel (1 mL) for about 2 minutes with a Vortex mixer at 3,400 rpm. The fraction of water phase in HIPE organogels was determined by control experiment. The control experiment was carried out as follows: After stirring the mixture of salt aqueous solutions (450 mL), THF (100 mL), toluene (98 mL) and methanol (2 mL) for 10 minutes, the mixture was separated into water and organic solvents with separating funnel, and

then the volumes of water and organic solvents were determined by a measuring cylinder. The fraction ( $f_w$ ) of water phase was calculated by  $f_w = V_w / (V_w + V_o)$  where  $V_w$  and  $V_o$  stand for the volumes of water phase and organic solvent phase, respectively.

**Fourier-transform infrared (FTIR) spectroscopy.** FTIR spectra were obtained with a Bruker Vertex 70 FTIR spectrometer. To prepare samples for FTIR measurement, THF solution of SSEBS was dropped onto KBr disk. For SSEBS/DAB-4, SSEBS/DAB-8 and SSEBS/DAB-16 organogels, newly formed gels after mixing the solutions of SSEBS in toluene/methanol (98/2, w/w) and PPI dendrimer in toluene were poured on KBr disks. The solvent was evaporated in fume hood first and then the disks were further dried under vacuum at 50 °C prior to measurement. PPI dendrimers were dropped onto KBr disks and measured directly. The spectra were recorded by the average of 32 scans in the standard wave number range of 600–4000  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$ .

**Rheological experiments.** Rheological experiments were taken on a TA DHR 3 rheometer with cone-plate geometry at 25 °C. A cone with a diameter of 40 mm and a tilt angle of 2° was used, and gap width was set to be 52  $\mu\text{m}$ . A solvent trap was used to minimize the effect of evaporation. Frequency sweeps with an angular frequency from 0.1 to 100 rad/s were performed at a strain of 5 %. For accuracy, the data from 0.5 to 100 rad/s were used.

**Conductivity measurement.** The conductivity of the organogels was determined on a SevenEasy conductivity meter (Mettler-Toledo GmbH, Switzerland) at room temperature. The conductivities of water and organic solvents were also studied for comparison, where water and organic solvents used were from the control experiment described above.

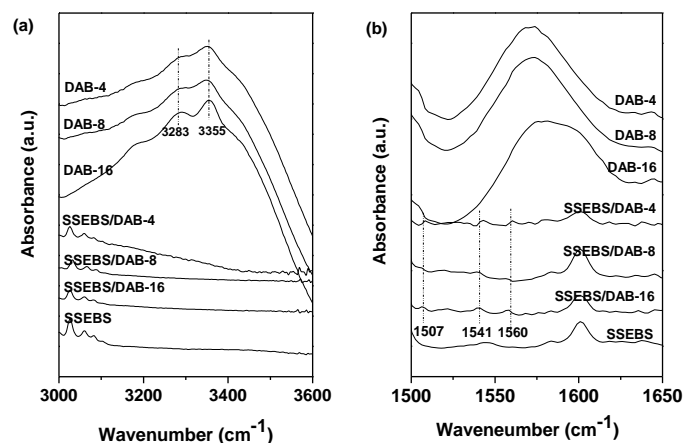
**Confocal microscopy.** Confocal imaging was performed on a laser scanning confocal microscope (Leica SP5, Leica Microsystems CMS GmbH, Germany). For observation, samples of HIPE organogels were prepared by mixing SSEBS/DAB-4, SSEBS/DAB-8 or SSEBS/DAB-16 organogels with 5% (w/v) pyrene in water/THF (4:1, v/v) on a Vortex mixer for 2 min, and then the so-formed gels were transferred onto glass slides. A laser with wavelength of 405 nm was used to excited pyrene in organic phase.

**Small-angle X-ray scattering (SAXS).** SAXS experiments were conducted at the Australian Synchrotron on the small/wide-angle X-ray scattering beamline. For SSEBS solution, SSEBS/DAB-4 and SSEBS/DAB-16 organogels, the samples were put into 1.0 mm quartz capillaries. The background correction was carried out by measuring the scattering of an empty capillary and correcting for sample absorption. For HIPE organogels, the samples were put into a multiwall plate, and the background correction was with same solvent used.

## 2. Ionic interaction between SSEBS and PPI dendrimer

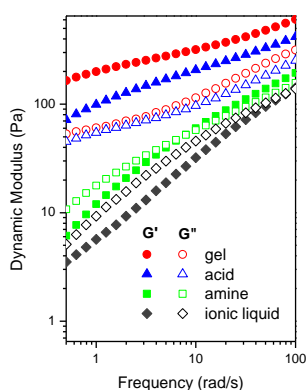
FTIR spectroscopy was applied to study the ionic interaction between SSEBS and PPI dendrimers in organogels after evaporation of solvents. Fig. S2 presents the FTIR spectra of these

morganogels. Fig S2(a) shows two characteristic peaks at 3283 and 3355  $\text{cm}^{-1}$ , attributable to symmetric and asymmetric stretching vibrations of  $-\text{NH}_2$  in the PPI dendrimer (DAB-4, DAB-8 and DAB-16), respectively.<sup>2</sup> These two peaks are completely suppressed in the SSEBS/DAB-4, SSEBS/DAB-8 or SSEBS/DAB-16 organogels, indicative of disappearance of the amine groups due to formation of the protonated amine moieties that exhibit characteristic peaks observed at 1507, 1541 and 1560  $\text{cm}^{-1}$ .<sup>3</sup> This is in accordance with the ionic interactions observed between sulfonic acid groups and amine moieties in our previous studies on blends of triblock ionomer SSEBS.<sup>1,4</sup>



**Fig. S2** FTIR spectra of SSEBS/PPI dendrimers organogels after evaporation of solvents in the range of (a) 3000 - 3600  $\text{cm}^{-1}$  and (b) 1500 - 1650  $\text{cm}^{-1}$ .

### 3. Responsiveness of organogels



**Fig. S3** Dynamic moduli  $G'$  (filled) and  $G''$  (hollow) of organogels from SSEBS/DAB-4 with 0.5% of acid, amine and salt as a function of oscillatory shear frequency.

The responsiveness of the pre-formed organogels was investigated with rheological measurement, and the results of dynamic frequency measurements for pre-formed organogels with 0.5% (v/v) of acetic acid, triethylamine and their salt are shown in Fig. 3. It is noted that both elastic moduli  $G'$  and

viscous moduli  $G''$  decrease with the addition of acid to the pre-formed gels although the  $G'$  remain higher than the corresponding  $G''$ , indicating the existence of the three-dimensional network. A crossover appears between the  $G'$  and the corresponding  $G''$  for the organogels with amine or salt, showing liquid-like behaviour in the low frequency before the crossover.

#### 4. Movies

Two short movies are available to show (a) organogel formation: a typical process for gel formation upon mixing SSEBS and PPI dendrimer solution and (b) HIPE organogel formation: a typical process for HIPE organogel formation from pre-formed gel.

#### 5. References

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