

# High internal phase emulsion (HIPE) xerogels for enhanced oil spill recovery

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## 1. Experimental section

**Materials.** Three kinds of polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (SEBS) with 28, 42 and 68 mol % polystyrene blocks were bought from Sigma-Aldrich. Polypropylenimine (PPI) dendrimers of generation 2 were supplied by Sigma-Aldrich and used as received. Other chemicals such as 1,2-dichloroethane (DCE), toluene, methanol, tetrahydrofuran (THF), NaCl, acetic anhydride, concentrated sulfuric acid (96%), diethyl ether, isopropyl alcohol (IPA) were of reagent grade. Water used in this work was distilled water.

**Preparation of sulfonated polystyrene-block-poly(ethylene-ranbutylene)-block-polystyrene (SSEBS).** Sulfonation of SEBS (SSEBS) was prepared from SEBS according to the procedure in previous reports.<sup>1, 2</sup> In brief, fresh acetyl sulfonate was prepared from acetic anhydride and concentrated sulfuric acid in DCE. Then SEBS was dissolved in DCE under 50-55 °C in a nitrogen atmosphere and the as-prepared acetyl sulfonate was added into the solution. The mixture was continuously stirred for 4 hours and the reaction was stopped after injecting 10 mL of IPA. The mixture containing SSEBS was poured into boiling water and subsequently washed with cold deionized water several times until the pH of the solution became neutral. Then SSEBS was obtained after drying under vacuum at 60 °C for 2 days.

The sulfonation degree of SSEBS was tested by titration method which was described detailed in our previous work.<sup>2</sup> And the titration results showed that the sulfonation degrees of SSEBS samples prepared from SEBS with 28, 42 and 68 mol % polystyrene blocks were 15, 13.3 and 11.6%, respectively.

**Preparation of HIPE organogels.** HIPE organogels were prepared according to the route reported in our previous work.<sup>1</sup> In typical, 2 % (w/v) of PPI dendrimers in toluene was mixed with 5 % (w/v) of SSEBS solution in toluene and methanol (v/v, 98:2) and then the mixture was stirred acutely to form organogels. Subsequently, tetrahydrofuran and 1M aqueous NaCl solutions were added to the pre-formed organogels, and after shearing the mixture for 5 minutes with a Vortex mixer at 3,400rpm, HIPE organogels were obtained.

**Preparation of HIPE xerogels.** The as-prepared HIPE organogels were dispersed into diethyl ether under stirring. Then the mixture was poured into huge volume of water under vigorous stirring and filtered after stirring for 2 hours. The HIPE xerogels were obtained by freeze drying for 24 hours.

**Characterization of oil absorption performance.** The oil absorption performance of HIPE xerogels can be characterized by oil absorption capacity, absorption rates and reused property of the oil absorbents.<sup>3</sup>

The mass absorption capacity can be defined as  $(m_s - m_0)/m_0$ , where  $m_0$  and  $m_s$  represent the weights of the xerogels before and after oil-absorption, respectively. A known weight of HIPE xerogels ( $m_0$ ) were put into a beaker containing oil or organic liquid and left quiescent for overnight. Then the xerogels were lifted and dried to remove residual surface oil/organic liquid before recording the weight of  $m_s$ . The oil absorption capacity can be calculated from the above equation.<sup>4</sup>

The absorption rate of HIPE xerogels was investigated by putting a certain weight of HIPE xerogels ( $m_0$ ) into the oil or organic liquid, then monitoring the weight changing of xerogels ( $m_t$ ) with time. The weight gained of HIPE xerogels at time  $t$  was defined as  $((m_t - m_0)/m_0)$ .<sup>5</sup>

The reused property of HIPE xerogels was carried out by simple mechanical squeeze, and the absorbed oil or organic liquid was recovered from the xerogels. The recovery was calculated as  $m_{re}/(m_s - m_0)$ , where  $m_{re}$  is the weight of the recovered oil or organic liquid,  $m_s$  is the swollen xerogels weight (g) at the saturated absorption state and  $m_0$  is the initial weight of the xerogels.<sup>6</sup>

The water absorption capacity was tested according to the approach for the determination of the oil absorption capacity. The initial weight of HIPE xerogels was measured as  $m_0$ . Then, the xerogels were put on the surface of distilled water, 0.5M NaCl aqueous solution and sea water, and after absorption for 2 hours, the weights of the xerogels were recorded as  $m_w$ . The water absorption capacity can be deduced through  $(m_w - m_0)/m_0$ .<sup>3</sup>

**Characterizations.** Confocal imaging of HIPE organogels was performed on a laser scanning confocal microscope (Leica SP5, Leica Microsystems CMS GmbH, Germany). The porous structure of HIPE xerogels was observed using a Neoscope JCM-5000 SEM (JEOL, Japan). Contact angle was tested on a KSV CAM 101 contact angle instrument.

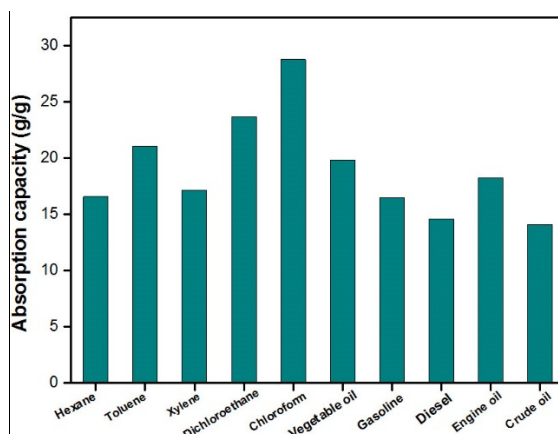
## 2. Oil absorption comparison of different absorbents

Table S1. Comparison of absorption capacities of absorbents

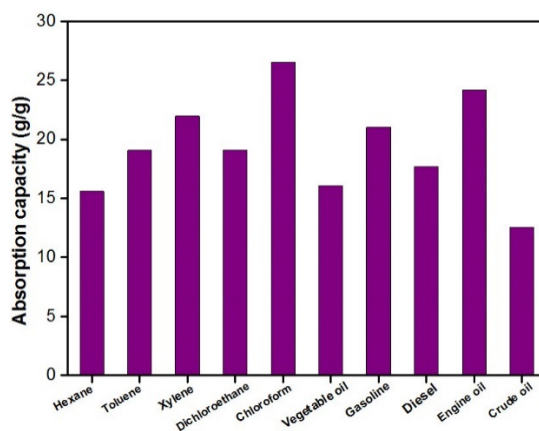
absorbents	Oils or solvents and absorption capacities (g/g)	References
Phase-selective xerogels	gasoline (5.83), diesel (4.59)	14
Lignin-based xerogels	gasoline (c.a. 2.1), toluene(c.a. 2.5)	23

Polystyrene HIPE xerogels	gasoline (16.49), n-hexane (4.45), mineral ether (5.02), kerosene (6.19), benzene (18.71), dichloromethane (20.21), salad oil (2.75), machine oil (2.51)	15
Poly (tertiary-butylmethacrylate) HIPE xerogels	kerosene (8.17), benzene (15.37), dichloromethane (17.33), used oil (4.98)	16
Polymeric sponges	diesel (c.a. 40)	24
Polymethylsilsesquioxane xerogels	kerosene (c.a. 7.8), toluene (c.a. 8.5)	25
Polymer SEBS HIPE xerogels	gasoline (21.2), diesel (23.8), dichloroethane (22.6), toluene (22.3)	This work

### 3. Absorption capacities of the HIPE xerogels



**Fig. S1** Absorption capacities of HIPE xerogels based on SEBS with 28 mol % polystyrene blocks for organic solvents and oils.



**Fig. S2** Absorption capacities of HIPE xerogels based on SEBS with 68 mol % polystyrene blocks for organic solvents and oils.

#### 4. Absorption-squeeze process of HIPE xerogels

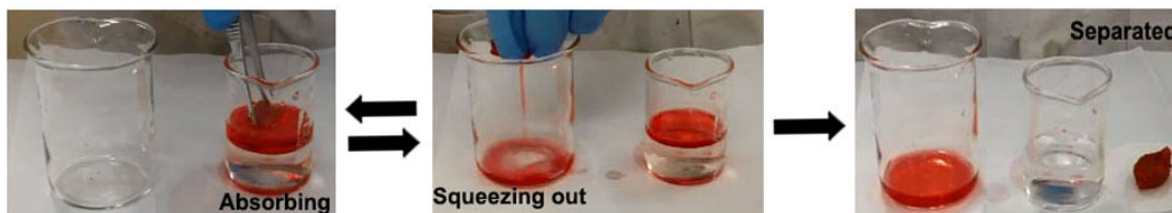


Fig. S3 Absorption-squeeze process of HIPE xerogels separating diesel from water.

#### 5. Water absorption capacity of HIPE xerogels

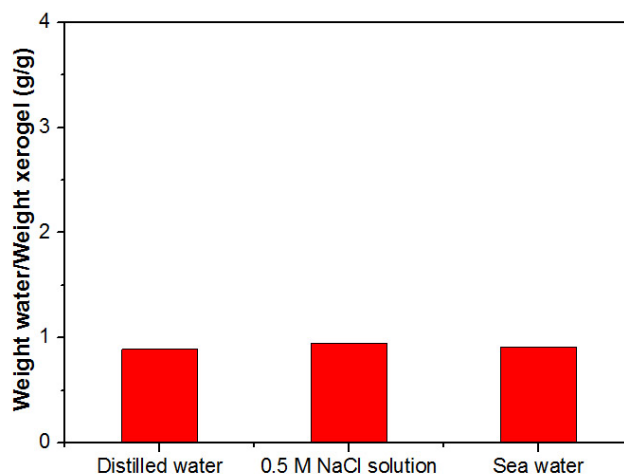


Fig. S4 Water absorption of HIPE xerogels in distilled water, 0.5M NaCl solution and sea water.

#### 6. Movie

The movie shows the process of HIPE xerogels absorbing oil from the surface of water.

#### 7. References

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