

**Fabrication of free-standing membranes with tunable pore structures
based on the combination of electrospinning and self-assembly of
block copolymer**

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EXPERIMENTAL

Materials

Styrene and 2-vinyl pyridine were purchased from Alfa Aesar. Azodiisobutyronitrile (AIBN) was obtained from J&K Scientific Ltd. Carbon disulfide and ethanethiol were purchased from Beijing Coupling Technology Co., Ltd. Trioctyl methyl ammonium chloride was obtained from TCI (Shanghai) Development Co., Ltd. Sodium hydroxide was purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. Methanol, n-hexane, acetone, ethyl acetate, trichloromethane, concentrated hydrochloric acid and tetrahydrofuran (THF) were purchased from Beijing Chemical Reagents Company. Styrene and 2-vinyl pyridine were distilled in vacuum before prior to use. THF, acetone, trichloromethane, ethanethiol and carbon disulfide were distilled under normal pressure. AIBN was recrystallized three times from ethanol. The other reagents were used as received.

Synthesis of S-Ethyl- S'-(α,α' -dimethyl- α'' -acetic acid) trithiocarbonate (EMDAT)

The target compound was prepared by the method described according to the report¹.

Synthesis of PS-b-P2VP Diblock Copolymer

PS-b-P2VP was synthesized via reversible addition fragmentation chain transfer (RAFT) polymerization. Firstly, PS-CTA macromolecular chain transfer agent was synthesized by polymerizing styrene in a sealed ampule equipped with a stir bar under vacuum. A typical procedure was as follows: styrene, EMDAT and AIBN with a certain molar ratio were added into a 10 mL glass ampule. The mixture was degassed through three freeze-evacuate-thaw cycles, and then the ampule was sealed under vacuum. The polymerization was carried out in an oil bath at 90 °C in a well-defined predetermined time. The resulted crude product was purified by precipitating into a large amount of methanol three times. Monomer conversion was determined by the ¹H NMR spectrum. Next, PS-CTA was used as macro RAFT-agents to synthesize PS-b-P2VP. A general procedure: PS-CTA, 2-vinylpyridine and AIBN were charged into a 10 mL Schlenk flask. The mixture was degassed by three freeze-evacuate-thaw cycles and then flame-sealed under vacuum. Polymerization was carried out in an oil bath thermostated at 60 °C for a certain period of time. The resulting product dissolved in THF was purified by precipitating in hexane three times. The composition was determined by the ¹H NMR spectrum.

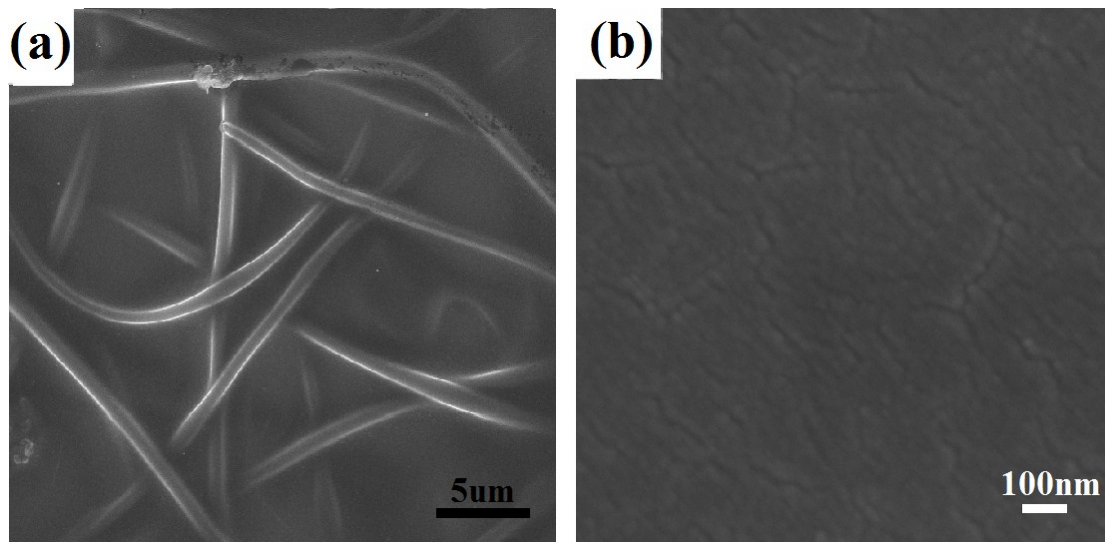


FIGURE S1 SEM images of composite membrane composed of as-prepared electrospun PVA/SiO₂ membrane and PS-b-P2VP at different level of magnification.

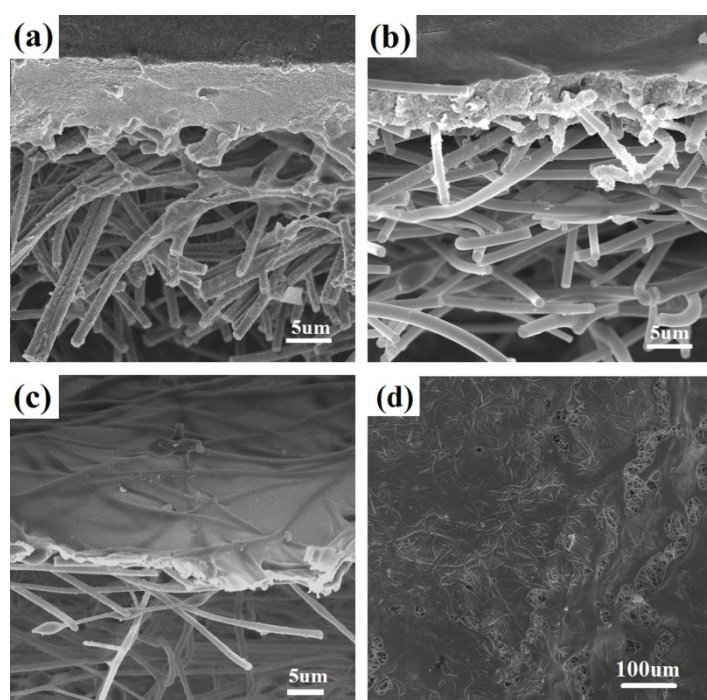


FIGURE S2 SEM images of cross-sectional view of asymmetric membranes with separation layer prepared from (a) 3 wt% ; (b) 2 wt%; (c) 1 wt% of PS-b-P2VP solution; (d) SEM image of the top view of asymmetric membranes with separation layer prepared from 1% PS-b-P2VP solution.

REFERENCES

1. A. J. Convertine, B. S. Lokitz, Y. Vasileva, L. J. Myrick, C. W. Scales, A. B. Lowe and C. L. McCormick, *Macromolecules* 2006, **39**, 1724-1730.