

Electronic Supplementary Material (ESI) for NJC.

Experimental section

Chemicals

Pyromellitic dianhydride (PMDA, $\geq 99\%$) and 4,4'-diaminodiphenyl ether (ODA, $\geq 99\%$, Forsman) were purchased from Forsman Scientific (Beijing) Co., Ltd. Anhydrous N, N-dimethylacetamide (DMAc, $\geq 99\%$), α -bromoisobutyryl bromide (BIBB, 98%), trifluoroacetic Acid (TFA, 99%), 1,4-Dioxane (99.5%), copper (II) Bromide (CuBr_2 , 99%), triethylamine ($\geq 99.5\%$), N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, 98%) and bis(tert-butoxycarbonyl)oxide ($(\text{Boc})_2\text{O}$, 99%) were provided by Shanghai Macklin Biochemical Technology Co., Ltd and used as received. Hydrazine monohydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, 80%), stannous octoate ($\text{Sn}(\text{Oct})_2$, 97%) and ethylenediamine (EDA, 99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Styrene (St, 98%, Aldrich) was distilled under reduced pressure before use. PMDA was dried at 125 °C in a vacuum for 24h before use. All other reagents were used without further purification.

Characterization

Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) was performed using a TG209F3 instrument thermal analyzer system (Netzsch) at heating rate of 10 °C/ min under the N_2 condition with a flow rate of 50 mL/ min.

Gel Permeation Chromatography

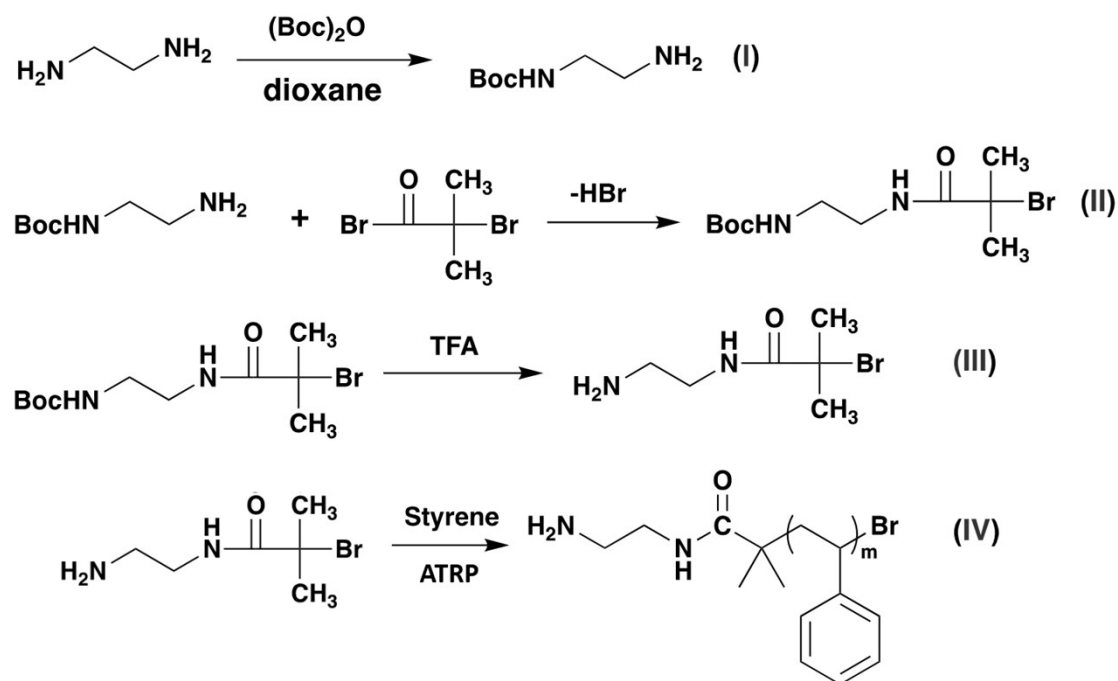
Polymers were well dissolved in tetrahydrofuran (THF) at a concentration of 0.2 wt % and passed through a 0.45 μm Teflon syringe filter to remove possible particles. The gel permeation chromatography (GPC) is equipped with three columns (PL-gel 5 μ , 30 cm mixed-C, Polymer Laboratories) at 35 °C with a flow rate of 1 mL/min as mobile phase. The elution time was detected by Waters 2414 Refractive Index Detector. The molecular weight and polydispersity were calculated by the Water Breeze software. Calibration was performed using narrow distribution polystyrene standards (Polymer Laboratories).

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were recorded at a resolution of 1 cm^{-1} with a Nicolet 380 spectrometer.

Field-Emission Scanning Electron Microscopy (FE-SEM)

The FE-SEM was performed on a MERLIN Compact, Zeiss using accelerating voltages of 20 to 3keV. The sample were treated with gold spray.



Scheme S1 synthetic route of PS-NH₂ (narrow PDI)

Scheme S1 shows a schematic diagram of the procedure to synthesize PS-NH₂ with a narrow PDI.

Synthesis of *tert*-butyl (2-aminoethyl) carbamate (I)

The synthesis was conducted according to Vo et al^[1]: A solution of 6.55 g (Boc)₂O (0.03 mol) in 75 mL dioxane was added in 5 h to a vigorous stirred solution of ethylenediamine (13.95 g, 0.23 mol) in 75 mL dioxane at room temperature. After 20 h of stirring at room temperature, a small amount of byproduct bis(*N,N*-*tert*-butyloxycarbonyl)-1,2-diaminoethane was removed by filtration. The filtrate was concentrated by vacuum distillation to remove excess of solvent and unreacted ethylenediamine. The subsequent dropwise addition of 500 mL water precipitated bis(*N,N*-*tert*-butyloxycarbonyl)-1,2-diaminoethane, which was filtered off. The resulting aqueous solution was saturated with sodium chloride and extracted with dichloromethane. The organic phase was collected, dried over anhydrous magnesium sulfate, and evaporated to give product (I).

Synthesis of *tert*-butyl (2-(2-bromo-2-methylpropanamido)ethyl) carbamate (II)

2.64 g (0.0165 mol) of product (I) was dissolved in 30 mL of dichloromethane under N₂ atmosphere in a reaction flask. The solution was cooled to 0 °C and 1.67 g (0.165 mol) of triethylamine was added while the flask was kept in an ice-water bath. 3.795 g (0.0165 mol) of 2-bromoisobutyryl bromide was slowly added dropwise to the reaction flask in 30 min and the reaction mixture was stirred at room temperature for 48 h. The final mixture was filtered and the white precipitate was washed 3 times with ice-cold *n*-hexane. The filtration was distilled under vacuum and the obtained powder was re-

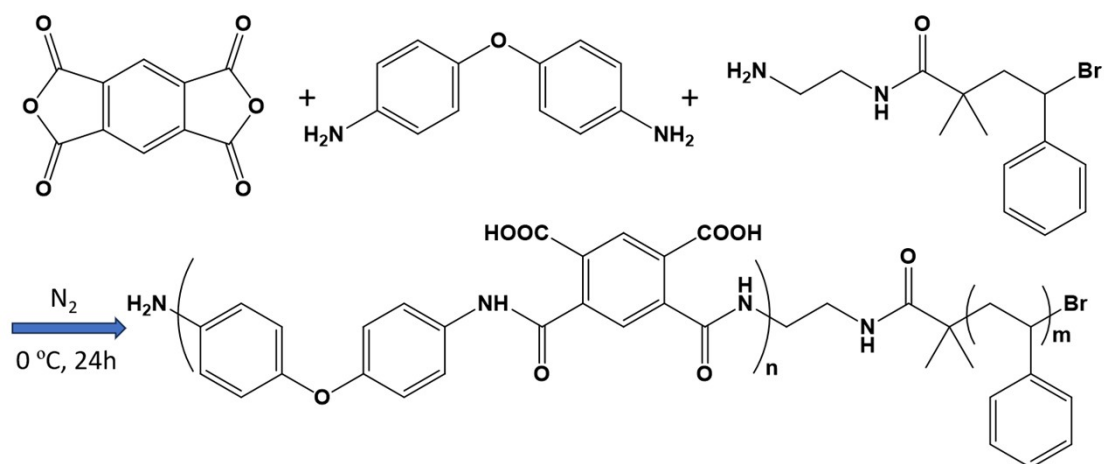
crystallized 3 times in *n*-hexane. Finally, product (II) was obtained after vacuum drying at 40 °C.

Synthesis of *N*-(2-aminoethyl)-2-bromo-2-methylpropanamide (ATRP-NH₂, III)

Product (II) (2g, 6.4mmol) was dissolved in DCM (10 ml) in a reaction flask and 2.4 mL (32 mmol) of TFA was added. The solution was left to be stirred at room temperature for 24 h and extracted 3 times by NaHCO₃ aqueous solution (w=10%, 30 ml); then deionized water was used to extract organic layer until aqueous phase becomes neutral. The organic layer was dried overnight with anhydrous magnesium sulfate; after removal of magnesium sulfate, the dried organic solution was distilled under vacuum and the white solid product (III) ATRP-NH₂ was obtained.

Synthesis of PS-NH₂ (IV)

Amino-terminated polystyrene (PS-NH₂) was synthesized using atom transfer radical polymerization (ATRP). Typically, ATRP-NH₂ (0.1045 g, 0.0005mol) and styrene (13.55 g, 0.13mol) were added into a 100 mL Schlenk flask with a magnetic stirrer, then CuBr₂ (0.0223g, 0.0001 mol), Sn(Oct)₂ (0.0405g, 0.0001 mol) and PMDETA (0.0173 g, 0.0001 mol) were added to this stirred solution. After degassing by three freeze-evacuate-thaw and vent nitrogen cycles, the flask was sealed under high-purity nitrogen, the polymerization was carried out at 110°C for 24 h. The obtained bulk was dissolved in DCM and passed through a column of neutral alumina to remove the metal salt. After precipitation by adding polymer solution of DCM into 10-fold volume of ethanol, the precipitate was collected by filtration and dried under vacuum at 60 °C overnight. The white powdered PS-NH₂ (IV) was acquired.



Scheme S2 preparation of PAA-*b*-PS

Scheme S2 presents the process for preparation of PAA-*b*-PS.

Synthesis of PAA-*b*-PS

ODA and moderate amount of PS-NH₂ were firstly stirred with DMAc in a 250 ml three-necked flask until a homogeneous solution forms; then PMDA was added in several batches. The specific feed ratio is presented in Table S1. The mixture was continuously stirred at 0 °C for 24 h under nitrogen atmosphere. Three PAA-*b*-PS

solutions with concentration 5 wt% were finally prepared and stored in a refrigerator prior to use.

Fabrication porous PI films

The above three DMAc solutions of PAA-*b*-PS were casted on a glass substrate. The solvent was removed in a vacuum oven at 50 °C for 8 h. The dried PAA-*b*-PS films were thermally treated under a flowing nitrogen atmosphere in sequential procedure: heated up to 100 °C in 30 min and kept at 100 °C for 1 h → heated up to 200 °C in 30 min and kept at 200 °C for 1 h → heated up to 350 °C in 50 min and kept at 350 °C for 4 h → cooled to room temperature naturally. Finally, the porous PI films was soaked in hot water and peeled off the glass substrate.

Table S1 the feed ratio of PAA-*b*-PS

	n(PMDA): n(ODA): n(PS-NH ₂)	$\bar{M}_n(\text{PS})$ /g•mol ⁻¹	^c $\bar{M}_{n,th}(\text{PAA})$ /g•mol ⁻¹	^d $\bar{M}_{n,th}(\text{PAA-}b\text{-PS})$ /g•mol ⁻¹	^e f_{PS}^V
PAA- <i>b</i> -PS-1	1: 1: 0.00552 ^a	^a 25200	75900	101100	30%
PAA- <i>b</i> -PS-2	1: 1: 0.01385 ^a	^a 25200	37900	63100	46%
PAA- <i>b</i> -PS-3	1: 1: 0.01666 ^a	^a 25200	25300	50500	56%
PAA- <i>b</i> -PS-4	1: 1: 0.00988 ^b	^b 28300	42500	70800	46%

a, PDI = 1.22; b, PDI = 5.47 (recorded by GPC);

c, $\bar{M}_{n,th}(\text{PAA})$ was calculated using equation (1):

$$\bar{M}_{n,th}(\text{PAA}) = \frac{\bar{X}_n}{2} \times M_{repeat} \quad (1)$$

where \bar{X}_n is degree of polymerization and is calculated according to equation (2) in which r represents stoichiometric functional groups ratio of initial two monomers ($r \leq 1$); p represents the extent of reaction. Here, p value is close to 1 because of high reactivity between dianhydride and diamine, then equation (2) can be simplified as equation (3):

$$\bar{X}_n = \frac{1+r}{1+r-2rp} \quad \#(2)$$

$$\bar{X}_n = \frac{1+r}{1-r} \quad \#(3)$$

M_{repeat} is 418 which is molecular weight of repeat unit of PAA.

d, $\bar{M}_{n,th}(\text{PAA-}b\text{-PS})$ is sum of $\bar{M}_{n,th}(\text{PAA})$ and $\bar{M}_n(\text{PS})$.

e, f_{PS}^V was acquired by equation (4):

$$f_{PS}^V = \frac{\frac{\bar{M}_n(\text{PS})}{\rho_{PS}}}{\frac{\bar{M}_n(\text{PS})}{\rho_{PS}} + \frac{\bar{M}_{n,th}(\text{PAA})}{\rho_{PAA}}}$$

where $\rho_{PS} = 1.02 \text{ g/cm}^3$ [2] and $\rho_{PAA} = 1.33 \text{ g/cm}^3$ [3].

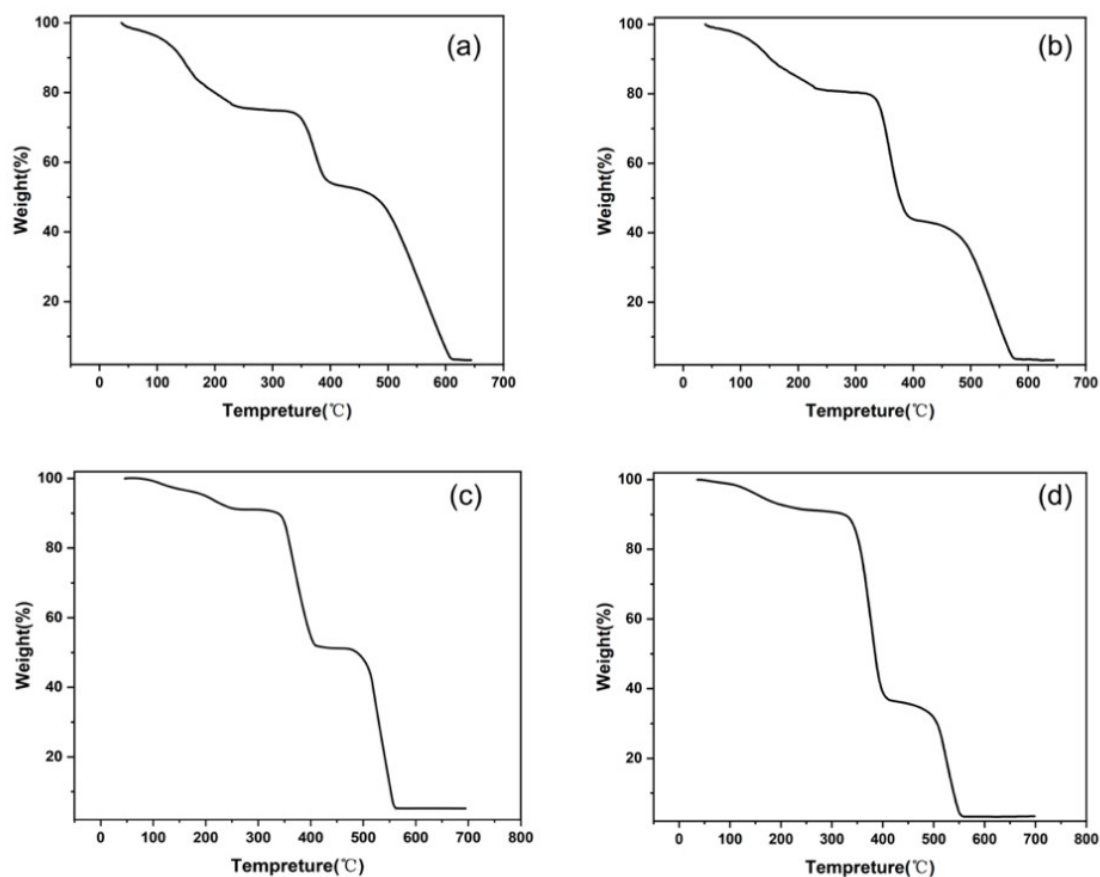


Fig. S1 TGA curves of PAA-*b*-PS with f_{PS}^V (a) 30%, (b) 46% and (c) 56% in which PDI of PS is 1.22; (d) is TGA curve of PAA-*b*-PS with f_{PS}^V 46% in which PDI of PS is 5.47.

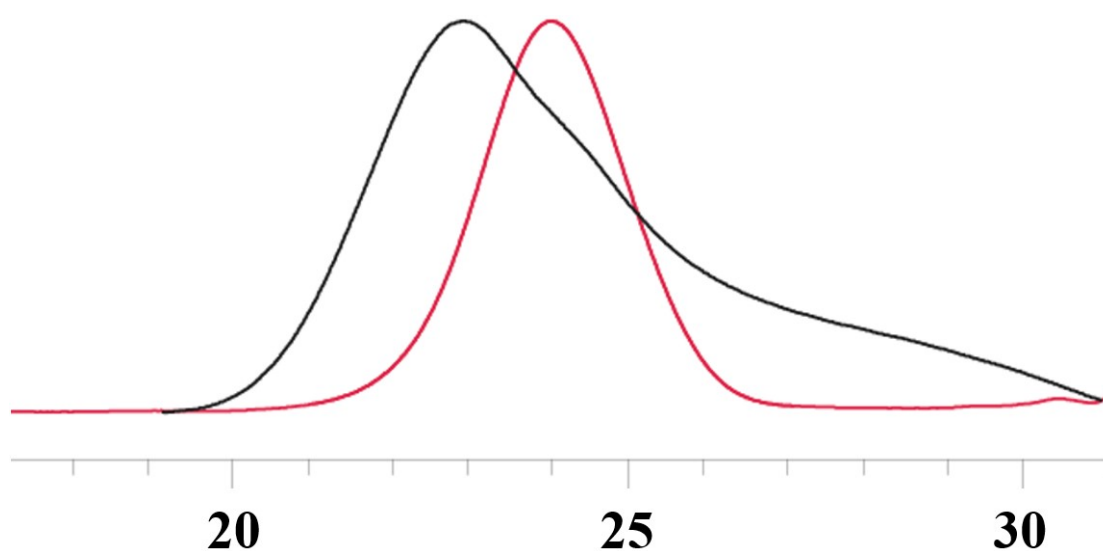


Fig. S2 GPC curves of the used two types of PS-NH₂

red: PDI = 1.22, $\bar{M}_n = 25200$ g/mol

black: PDI = 5.47, $\bar{M}_n = 28300$ g/mol

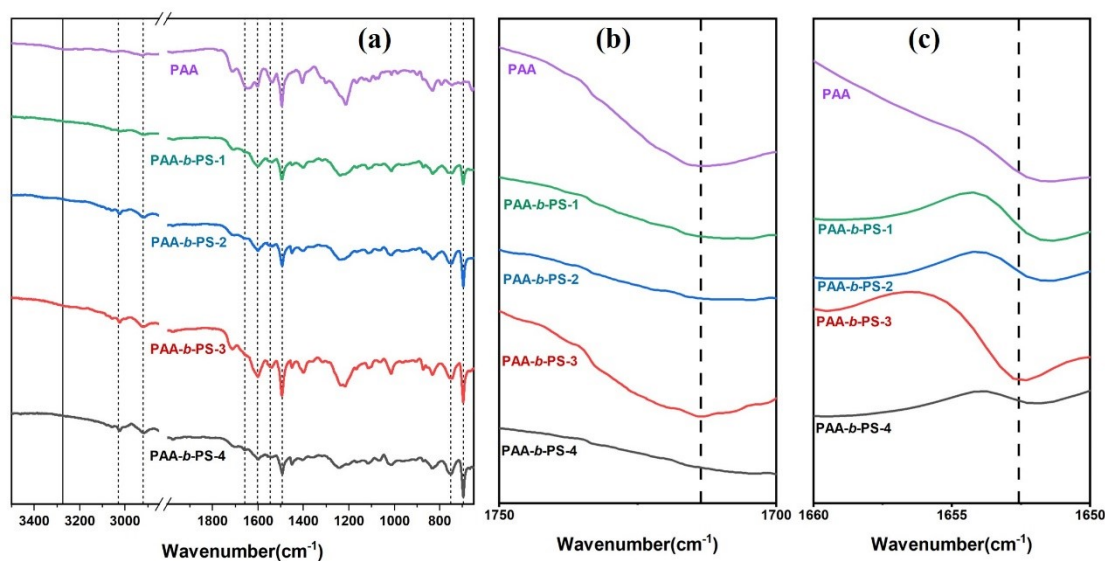


Fig. S3 FTIR spectra of PAA-*b*-PS: PS with PDI 1.22 is adopted in PAA-*b*-PS-1 ($f_{PS}^V = 30\%$), PAA-*b*-PS-2 ($f_{PS}^V = 46\%$) and PAA-*b*-PS-3 ($f_{PS}^V = 56\%$); PS with PDI 5.47 is adopted PAA-*b*-PS-4 ($f_{PS}^V = 46\%$). (a) is full spectrum; (b) and (c) are local enlarged spectra of (a).

The absorption bands at 696 cm^{-1} , 752 cm^{-1} , 1493 cm^{-1} , 1602 cm^{-1} , 3029 cm^{-1} are characteristic peaks of PS; the wavenumbers of 2915 cm^{-1} , 1714 cm^{-1} , 1658 cm^{-1} and 1546 cm^{-1} can be ascribed to the characteristic peak of carboxyl in -COOH, carbonyl absorption peaks in -COOH, carbonyl absorptions peak in -CONH- and C-N stretching vibration peak in -CONH, which are typical absorption peaks of PAA. Fig S3 (a) shows that the PAA-*b*-PSs were successfully prepared.

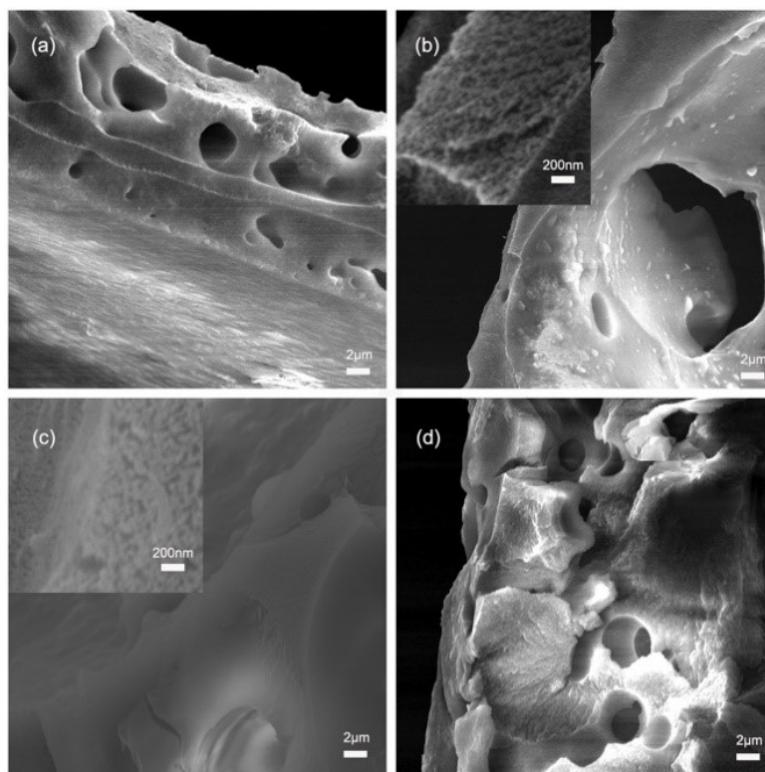


Fig. S4 Cross section of SEM images of PI films from (a) PAA-*b*-PS-1 ($f_{PS}^V = 30\%$), (b) PAA-*b*-PS-2 ($f_{PS}^V = 46\%$), (c) PAA-*b*-PS-3 ($f_{PS}^V = 56\%$) and (d) PAA-*b*-PS-4 ($f_{PS}^V = 46\%$) corresponding to those in **Fig. S3**. (Inset: higher-magnification images of the cross section)

References

- [1] C. D. Vo, D. Kuckling, H. J. P. Adler and M. Schohoff, *Colloid Polym. Sci.*, 2002, 280, 400-409.
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- [3] Y. Tsujita, H. Tanaka, H. Yoshimizu, T. Kinoshita, T. Abe and N. Kohtoh, *J. Appl. Polym. Sci.*, 1994, 54, 1297-1304.