

Electronic Supplementary Information for

Design of ionic liquid-based polyelectrolytes by combining 'nanostructurisation' and 'zwitterionisation'

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1. General procedures and materials

General procedures. ^1H NMR was obtained on a JNM-ECX400 and JNM-ECA500 (JEOL). Chemical shifts of ^1H signals were quoted to tetramethylsilane or 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt ($\delta = 0.00$) as internal standard. Elemental analysis was carried out on an Elementar Analytical vario EL3. Polydispersity were determined by SEC systems composed of degassing unit DGU-20A, durable pump LC-20AD, column oven CTO-20AC, UV-vis detector SPD-20A, refractive index detector RID-20A (Shimadzu), and column Asaphipak GF-7M HQ (shodex). SEC measurement was performed at 40 °C using DMF containing 10 mM LiBr or THF as an eluent at a flow rate of 0.4 ml/min. A calibration curve was prepared using polystyrene standard. Small angle X-ray scattering (SAXS) profiles were obtained using a Smart Lab (Rigaku) with $\text{CuK}\alpha$ radiation. Samples for transmission electron microscopy (TEM) were exposed to the vapor of 4 wt % of aqueous OsO_4 for 20 min and sectioned using an FC7 cryomicrotome (Leica) at -120 °C using a glass knife at 70 nm thickness. Sections were placed on Cu grids. TEM micrographs were obtained by JEM-2100 (JEOL) operating at 200 kV. The thermal properties were examined by DSC-6220 and TG/DTA-7200 (Seiko Instruments). The heating and cooling rates were 10 °C min^{-1} . The ionic conductivity was measured with an impedance analyzer Solartron 1260 (Schlumberger). The heating rate was 2 °C min^{-1} . Raman spectroscopy measurement was performed using JASCO NRS-1000 spectrometer with a liquid N_2 -cooled CCD detector and a Kaiser Optical holographic super-notch filter. For excitation, a Coherent Innova 90C Kr laser with a 20 mW beam at a 647.1 nm excitation wavelength was used.

Materials. All chemical reagents and solvents were obtained from commercial sources. Both styrene and 2-(dimethylamino)ethyl acrylate were distilled before use. AIBN was purified via recrystallisation. The other reagents were used without purification. All reactions were carried out in anhydrous solvents under an argon atmosphere.

2. Synthesis

Synthesis of PS

Styrene (52.8 g, 0.507 mol) and 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl] pentanoic acid (0.526 g, 1.30 mmol) were charged into a 200 mL Schlenk flask and subjected to three freeze-pump-thaw cycles. After stirring at 100 °C for 10 h, it was placed into liquid nitrogen. The product was purified by reprecipitation procedures with methanol and vacuum dried. Yield: 7.36 g of yellow powder. SEC (DMF containing 10 mM LiBr, 40 °C): $M_n = 3.39$ kg/mol, $M_w/M_n = 1.57$ (against PS standards). ^1H NMR spectrum was depicted in Fig. S1(a).

Synthesis of PS-*b*-PDMA-64.3

PS (1.00 g, 0.294 mmol), 2-(dimethylamino)ethyl acrylate (8.02 g, 56.0 mmol), AIBN (3.37 mg, 0.0205 mmol) and DMF (10 ml) were charged into a 30 ml Schlenk flask and subjected to three freeze-pump-thaw cycles. After stirring at 65 °C for 24 h, it was placed into liquid nitrogen. The product was purified by reprecipitation procedures with hexane and vacuum dried. Yield: 2.34 g of yellow oil. M_n and M_w/M_n determined by the combination of ^1H NMR and SEC measurement: $M_n = 10.8$ kg/mol, $M_w/M_n = 1.96$. Elemental analysis. Calcd: C, 67.9; H, 8.74; N, 6.84. Found: C, 67.7; H, 8.96; N, 6.53. ^1H NMR spectrum was depicted in Fig. S1(b).

Synthesis of PS-*b*-PZI-64.3

1, 3-propane sultone (4.45 g, 0.0364 mol), PS-*b*-PDMA-64.3 (0.663 g, 0.0614 mmol) and DMF (40 mL) were charged into a 100 ml Schlenk flask, which was stirred at 80 °C for 24 h. The product was purified by reprecipitation procedures with methanol and vacuum dried. Yield: 0.657 g of yellow powder. Elemental analysis. Calcd for PS-*b*-PZI H₂O per ZI unit: C, 51.0; H, 7.55; N, 4.09. Found: C, 49.5; H, 7.54; N, 3.93. ^1H NMR spectrum was depicted in Fig. S1(c).

Table S1. Molecular characteristics of polymers.

polymer	M_n (kg/mol) ^a	M_w/M_n ^b
Initial PS for PS- <i>b</i> -PDMA-19.7	12.4	1.32
PS- <i>b</i> -PDMA-19.7	16.4	1.36
Initial PS for PS- <i>b</i> -PDMA-44.1 and 64.3	3.39	1.57
PS- <i>b</i> -PDMA-44.1	6.64	-
PS- <i>b</i> -PDMA-64.3	10.8	1.96

^a Determined by ^1H NMR measurement and M_n for the initial PS determined by SEC measurement.

^b Determined by SEC measurement. -, not measured.

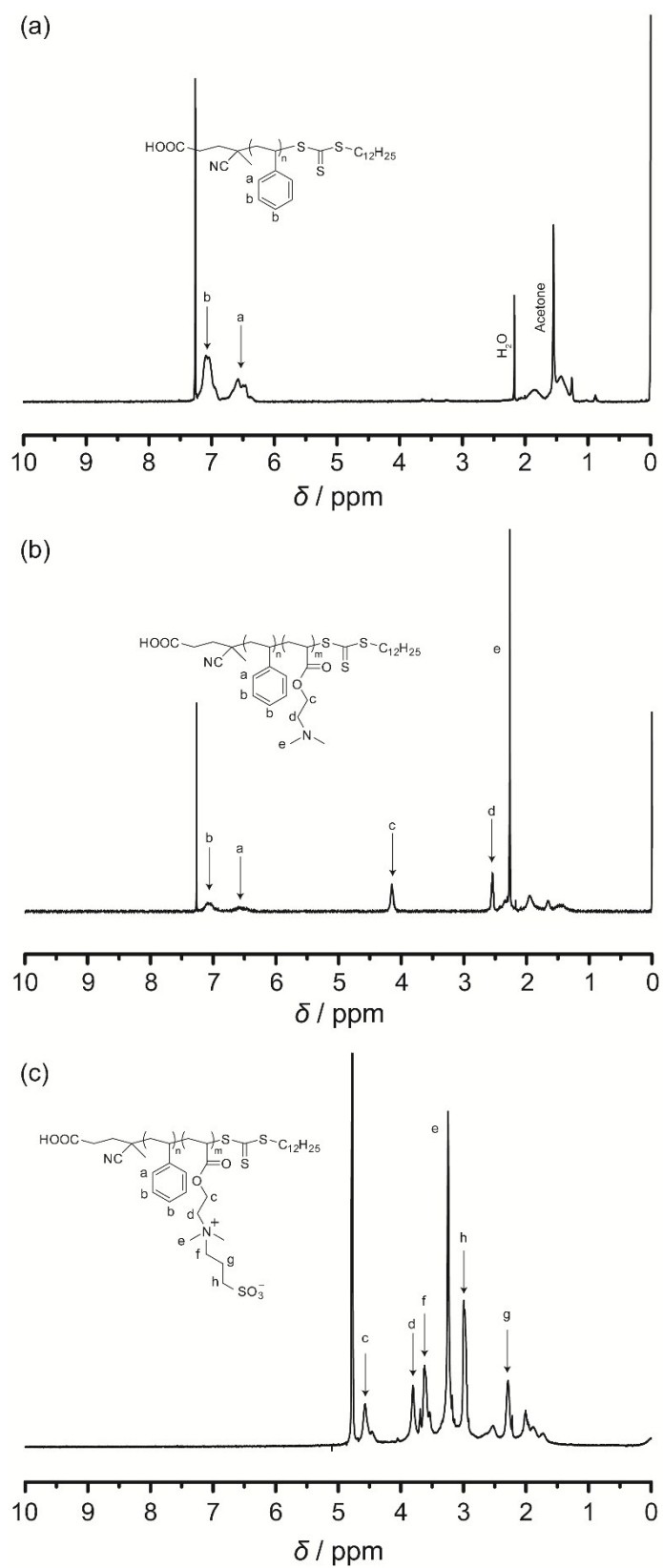


Fig. S1 ¹H NMR spectra of (a) PS in CDCl₃, (b) PS-*b*-PDMA-64.3 in CDCl₃ and PS-*b*-PZI-64.3 in D₂O. Fig. S1(c) is the same as Fig. 1(a) in the paper.

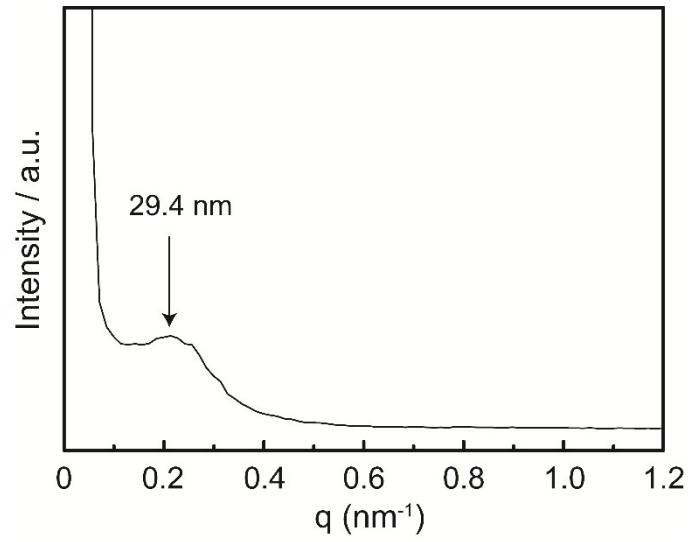


Fig. S2 SAXS profile of PS-*b*-PZI-64.3.

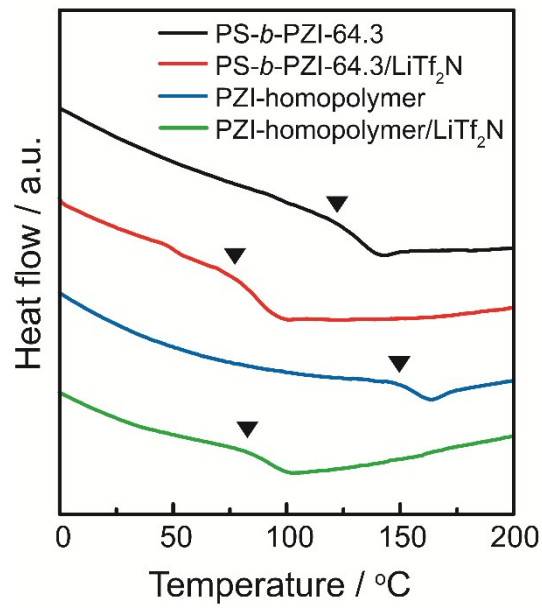


Fig. S3 DSC thermograms of the obtained samples on heating. Filled markers denote T_g .

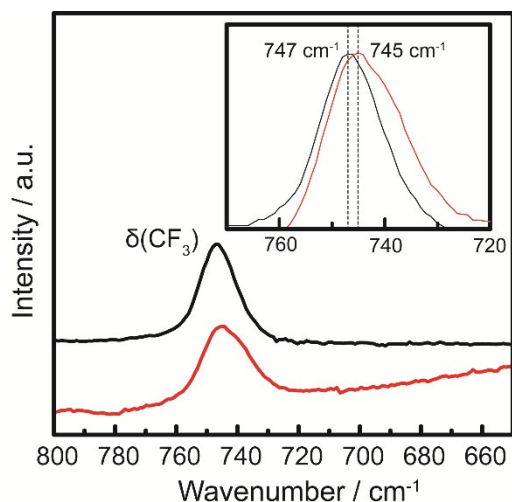


Fig. S4 Raman spectra of LiTf₂N (black) and PS-*b*-PZI-64.3/LiTf₂N (red).

Raman spectroscopy measurement has been frequently used for understanding the ion state of ionic liquids.¹ PS-*b*-PZI-64.3/LiTf₂N film showed a Raman band at 745 cm⁻¹, which was assigned to the symmetric bending vibration of the CF₃ group ($\delta_s(\text{CF}_3)$) of the Tf₂N, while the corresponding peak for LiTf₂N was observed at 747 cm⁻¹. The difference would be attributed to the dissociation of LiTf₂N in the PS-*b*-PZI-64.3/LiTf₂N film.

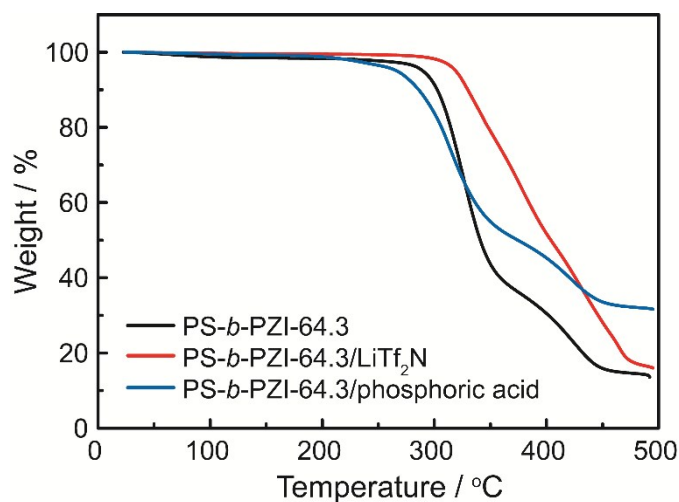


Fig. S5 TG curves of PS-*b*-PZI-64.3, PS-*b*-PZI-64.3/LiTf₂N and PS-*b*-PZI-64.3/phosphoric acid.

3. References

- (1) W. Ogihara, N. Suzuki, N. Nakamura and H. Ohno, *Polym. J.*, 2006, **38**, 117.