Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Nanoscale Layers of Precise Ion-Containing Polyamides with Lithiated Phenyl Sulfonate in the Polymer Backbone

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Synthesis of *m*PAS4Li

To an oven-dried 1 L round-bottom flask was added 2,4-diaminobenzenesulfonic acid (1.95 g, 10.36 mmol, 1 equiv.) under flowing N_2, followed by anhydrous *N*-methylpyrrolidone (NMP; 500 mL) and *N,N*-diisopropylethylamine (6.0 mL, 35.1 mmol, 3.4 equiv.). The solution was stirred under N_2 for approximately 30 minutes to fully dissolve the 2,4-diaminobenzenesulfonic acid. After complete dissolution of the solid, adipoyl chloride (1.5 mL, 10.24 mmol, 1 equiv.) was added to the flask under flowing N_2. The reaction was stirred at room temperature under an N_2 atmosphere for 72 hours. Upon completion, the reaction was concentrated by vacuum distillation to reduce the volume of NMP to approximately 100 mL. The solution was then transferred to 7K MWCO dialysis tubing and submerged in 1 L of deionized water for 24 hours. The tubing was then transferred to a 1 L solution of 25 g of LiCl in deionized water. After 24 hours, the aqueous LiCl solution was replaced with a fresh solution of 25 g of LiCl in 1 L of deionized water. This 24-hour ion exchange procedure was repeated three times in total. After the third ion exchange, the dialysis tubing was transferred to a large volume of deionized water, which was changed periodically over 7 days, to remove any remaining LiCl and fully purify the polymer product. The solution inside the dialysis tubing was then transferred to 50 mL centrifuge tubes, which were frozen in liquid nitrogen and lyophilized to yield a pale pink solid (0.187 g; 6% yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.43 (s, 1H), δ 10.02 (s, 1H), δ 8.36 (m, 1H), δ 7.53 (m, 2H), δ 2.32 (m, 4H), δ 1.64 (m, 4H).

Synthesis of *m*PAS5Li

To an oven-dried 250 mL round-bottom flask was added 2,4-diaminobenzenesulfonic acid (0.500 g, 2.66 mmol, 1 equiv.) under flowing N_2, followed by anhydrous *N*-methylpyrrolidone (NMP; 125 mL) and *N,N*-diisopropylethylamine (1.5 mL, 8.8 mmol, 3.3 equiv.). The solution was stirred under N_2 for approximately 30 minutes to fully dissolve the

2,4-diaminobenzenesulfonic acid. After complete dissolution of the solid, pimeloyl chloride (0.524 g, 2.66 mmol, 1 equiv.) was added to the flask under flowing N_2. The reaction was stirred at room temperature under an N_2 atmosphere for 72 hours. Upon completion, the reaction mixture was transferred to 7K MWCO dialysis tubing and submerged in 1 L of deionized water for 24 hours. The tubing was then transferred to a 1 L solution of 25 g of LiCl in deionized water. After 24 hours, the aqueous LiCl solution was replaced with a fresh solution of 25 g of LiCl in 1 L of deionized water. This 24-hour ion exchange procedure was repeated three times in total. After the third ion exchange, the dialysis tubing was transferred to a large volume of deionized water, which was changed periodically over 7 days, to remove any remaining LiCl and fully purify the polymer product. The solution inside the dialysis tubing was then transferred to 50 mL centrifuge tubes, which were frozen in liquid nitrogen and lyophilized to yield a white solid (0.163 g; 19% yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.42 (s, 1H), δ 9.99 (s, 1H), δ 8.37 (m, 1H), δ 7.52 (m, 2H), δ 2.28 (m, 4H), δ 1.61 (m, 4H), δ 1.35 (m, 2H).

Synthesis of *p*PAS4Li

To an oven-dried 250 mL round-bottom flask was added 2,5-diaminobenzenesulfonic acid (0.500 g, 2.66 mmol, 1 equiv.) under flowing N_2, followed by anhydrous *N*-methylpyrrolidone (NMP; 125 mL) and *N,N*-diisopropylethylamine (1.44 mL, 8.2 mmol, 3.1 equiv.). The solution was stirred under N_2 for approximately 1 hour to fully dissolve the 2,5-diaminobenzenesulfonic acid. After complete dissolution of the solid, adipoyl chloride (0.486 g, 2.66 mmol, 1 equiv.) was added to the flask under flowing N_2. The reaction was stirred at room temperature under an N_2 atmosphere for 72 hours. The reaction was then quenched with the addition of adipoyl chloride (0.243 g, 1.33 mmol, 0.5 equiv.) and was stirred for 2 hours at room temperature under an N_2 atmosphere. Anhydrous methanol (10 mL) was then added to

the reaction mixture under flowing N_2 and stirred at room temperature for 16 hours, in order to label the end groups with methyl esters. The reaction mixture was then transferred to 7K MWCO dialysis tubing and submerged in 1 L of deionized water for 24 hours. The tubing was then transferred to a 1 L solution of 25 g of LiCl in deionized water. After 24 hours, the aqueous LiCl solution was replaced with a fresh solution of 25 g of LiCl in 1 L of deionized water. This 24-hour ion exchange procedure was repeated three times in total. After the third ion exchange, the dialysis tubing was transferred to a large volume of deionized water, which was changed periodically over 7 days, to remove any remaining LiCl and fully purify the polymer product. The solution inside the dialysis tubing was then transferred to 50 mL centrifuge tubes, which were frozen in liquid nitrogen and lyophilized to yield a white solid (0.429 g; 53% yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.30 (s, 1H), δ 9.87 (s, 1H), δ 8.18 (m, 1H), δ 7.86 (m, 1H), δ 7.60 (m, 1H), δ 2.30 (m, 4H), δ 1.64 (m, 4H).

Synthesis of *p*PAS10Li

To an oven-dried 250 mL round-bottom flask was added 2,5-diaminobenzenesulfonic acid (0.500 g, 2.66 mmol, 1 equiv.) under flowing N_2, followed by anhydrous *N*-methylpyrrolidone (NMP; 125 mL) and *N,N*-diisopropylethylamine (1.44 mL, 8.2 mmol, 3.1 equiv.). The solution was stirred under N_2 for approximately 1 hour to fully dissolve the 2,5-diaminobenzenesulfonic acid. After complete dissolution of the solid, dodecanedioyl chloride (0.710 g, 2.66 mmol, 1 equiv.) was added to the flask under flowing N_2. The reaction was stirred at room temperature under an N_2 atmosphere for 72 hours. Upon completion, the reaction was exposed to air and quenched with the addition of deionized water (10 mL). The solution was stirred at room temperature for one hour, after which time LiCl (15 g) was added and the solution was stirred at room temperature for 16 hours. The reaction mixture was diluted with deionized water (20 mL) and transferred to 7K MWCO dialysis tubing, which was

suspended in 2 L of deionized water for 4 hours. A white precipitate that had formed inside the dialysis tubing was isolated by centrifugation, redissolved in a solution of LiCl (25 g) in NMP (100 mL), and stirred at room temperature for 16 hours. This solution was then transferred to 7K MWCO dialysis tubing and dialyzed against 2 L deionized water for 4 hours, during which time the polymer again precipitate inside the tubing. The sequence of isolation by centrifugation, overnight ion exchange in a LiCl/NMP solution, and dialysis against 2 L deionized water was repeated for the third time. After the third repetition, the dialysis water was replaced with 2 L of fresh deionized water, and the tubing was let dialyze for 48 hours. The white precipitate present in the tubing was then isolated by centrifugation, dissolved in 50 mL of NMP (with no LiCl added), transferred to 7K MWCO dialysis tubing, and dialyzed against 2 L of deionized water. No precipitate formed inside the tubing, indicating that after the Li^+ ion exchange is complete, pPAS10Li is soluble in water. The dialysis tubing was transferred to a large volume of deionized water, which was changed periodically over 7 days, to remove any remaining LiCl and fully purify the polymer product. The solution inside the dialysis tubing was then transferred to 50 mL centrifuge tubes, which were frozen in liquid nitrogen and lyophilized to yield 0.294 g of a pale pink solid (0.294 g; 28% yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.28 (s, 1H), δ 9.82 (s, 1H), δ 8.19 (m, 1H), δ 7.85 (m, 1H), δ 7.60 (m, 1H), δ 2.25 (m, 4H), δ 1.57 (m, 4H), δ 1.27 (m, 12H).

Synthesis of *p*PAS16Li

To an oven-dried 10 mL Schlenk flask was added 2,5-diaminobenzenesulfonic acid (1.25 g, 6.64 mmol) and 1,18-octadecanedioc acid (2.09 g, 6.64 mmol). The reactant mixture was then purged with N_2 for 24 h while stirring. After degassing, the reaction mixture was then placed in a preheated wax bath set to 130 °C while purging with N_2. After 1 h, the reaction temperature was increased to 195 °C and the mixture was stirred for 4 h under a

dynamic vacuum. Upon completion, the reaction mixture was dissolved in NMP/LiCl and transferred to 7K MWCO dialysis tubing, and submerged in 1 L of 0.1 M NH_4OH for 24 hours. The tubing was then transferred to a 1 L solution of 25 g of LiCl in deionized water. After 24 hours, the aqueous LiCl solution was replaced with a fresh solution of 10 g of LiCl in 1 L of deionized water. This 24-hour ion exchange procedure was repeated three times in total. After the third ion exchange, the dialysis tubing was transferred to a large volume of deionized water, which was changed periodically over 7 days, to remove any remaining LiCl and fully purify the polymer product. The solution inside the dialysis tubing was then transferred to 50 mL centrifuge tubes, which were frozen in liquid nitrogen and lyophilized. After lyophilization, the polymer powder was further purified by Soxhlet extraction with THF over 4 days followed by drying under vacuum to yield *p*PAS16Li as a purple solid (0.313 g; 10% yield).

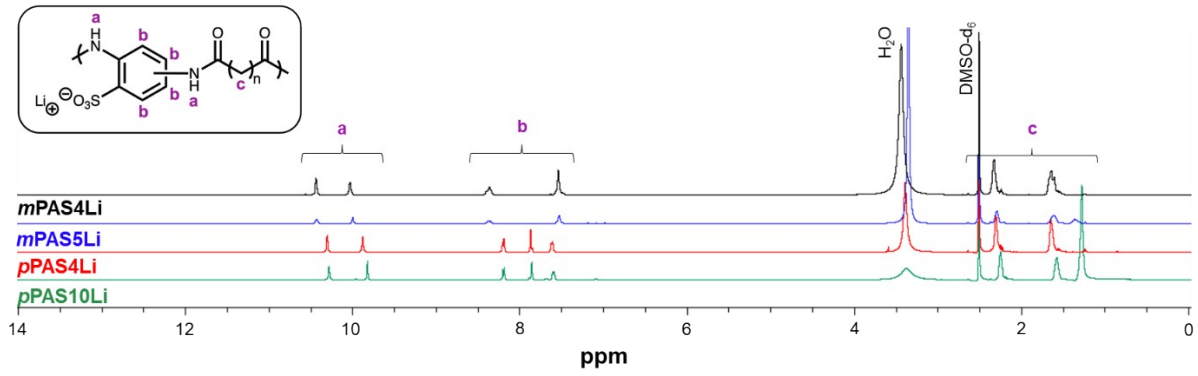

Figure S1. ^{1}H NMR spectra of *m*PAS4Li (black), *m*PAS5Li (blue), *p*PAS4Li (red), and *p*PAS10Li (green), showing amide protons (a), aromatic protons (b), and aliphatic protons (c) for each ionomer.

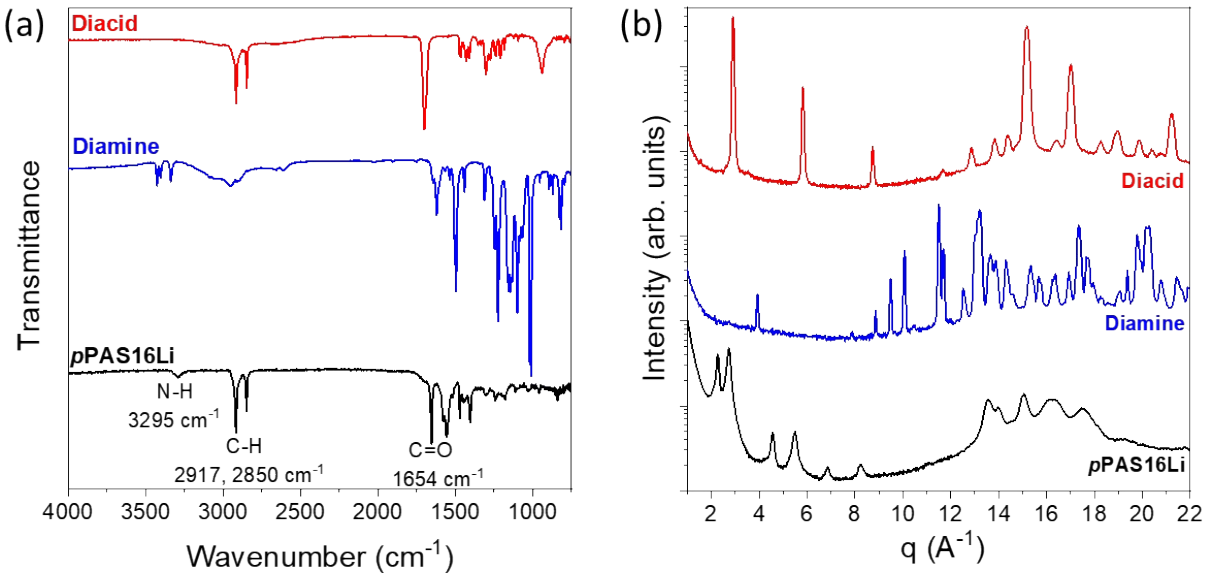

Figure S2. (a) Infrared spectroscopy spectrum and (b) X-ray scattering profile of 1,18-octadecanedioc acid (red), 2,5-diaminobenzenesulfonic acid (blue), and *p*PAS16Li.

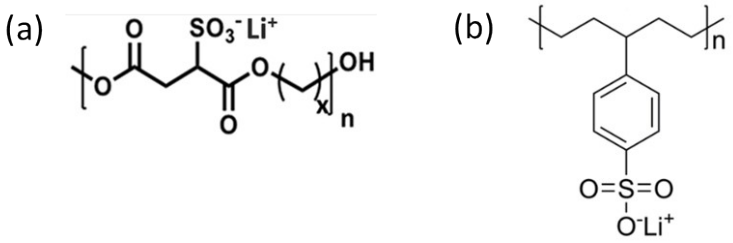

Figure S3. (a) Precise polyester sulfonates multiblock copolymers (PES*x*Li) and (b) a precise polyethylene with a phenyl sulfonate pendent to every 5th carbon (p5PhSA-Li).

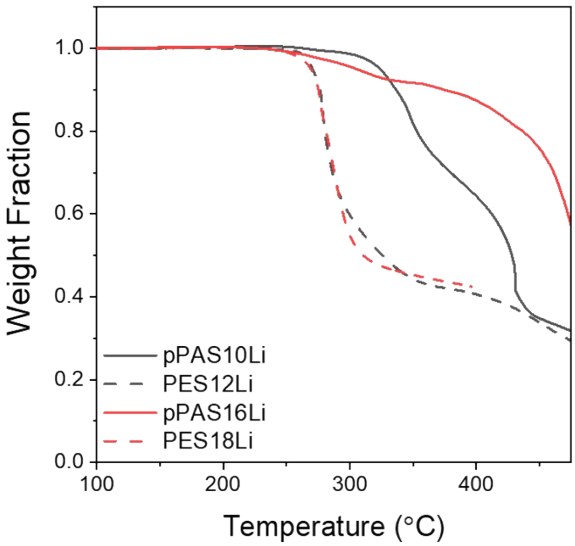

Figure S4. Comparison of thermogravimetric analysis traces of *p*PAS10Li and *p*PAS16Li with PES12Li and PES18Li, respectively. All data are collected at the same conditions under air and 10 °C/min ramping rate.

Equation for the random phase approximation of pPAS10Li

The effective Flory-Huggins interaction parameter (χ) of *p*PAS10Li is approximated by using the random phase approximation model. The X-ray scattering intensity of the linear $(AB)_n$ multiblock copolmyers with disordered phase is $I(q) = \frac{C}{1/i(q) - 2\chi}$, where *C* is a constant and *i(q)* is the intensity per repeating unit. The quantity $i(q)$ at $n > 20$ is

$$i(q) = N_v {f_{polar}}^2 (1 - f_{polar})^2 [\frac{2}{\lambda f_p (1 - f_{polar})} - \frac{2\left(1 - e^{-\lambda f_{polar}}\right)\left(1 - e^{-\lambda(1 - f_{polar})}\right)}{\lambda^2 {f_{polar}}^2 (1 - f_{polar})^2 (1 - e^{-\lambda})}]$$

where $\lambda = q^2 R_g^2$, and R_g is the radius of gyration of the repeating unit. Parameters of N_v and f_{polar} are volume-based degree of polymerization and volume fraction of polar blocks, respectively. The scattering intensities of *p*PAS10Li are fit with $I(q)$ and the variables of C, χ, and R_g.

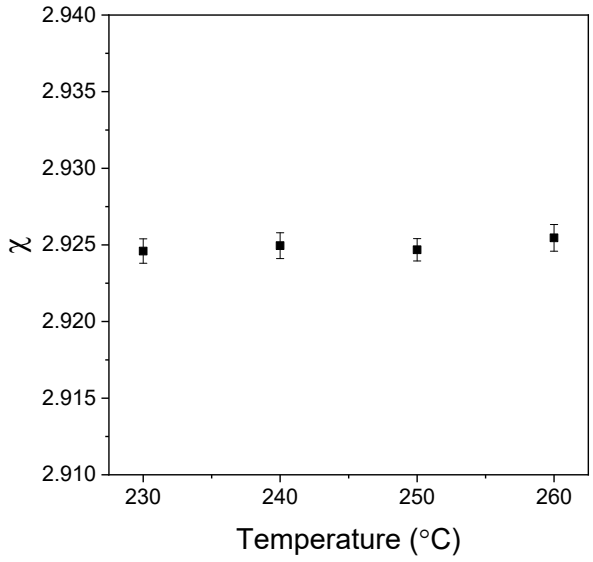

Figure S5. χ parameters as calculated from the scattering intensity of *p*PAS10Li at 230 – 260 °C using random phase approximation of multiblock copolymers.

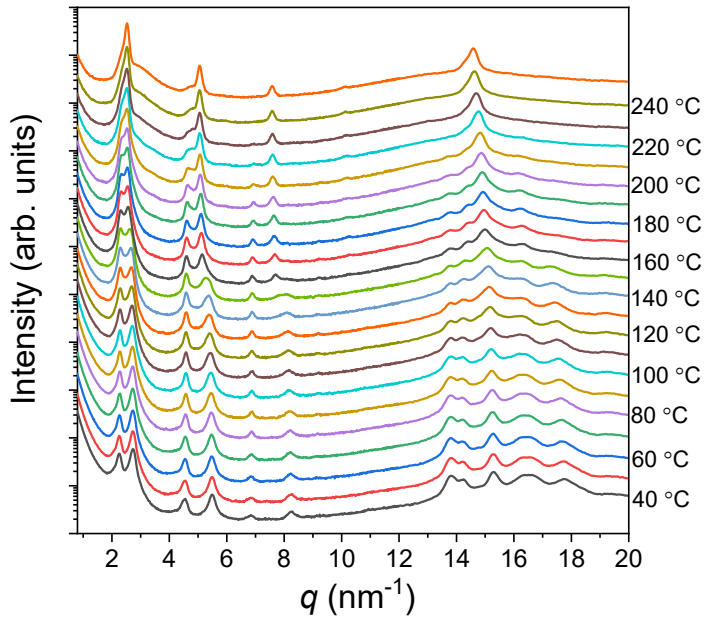

Figure S6. *In situ* X-ray scattering of *p*PAS16Li every 10 °C upon heating.