Supporting Information:

Inside the Ionic Aggregates Constrained by Covalently Attached Polymer Chain Segments: Order or Disorder?

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Experimental

Materials

A polystyrene (PS) (Mw ~ 192,000), propionic anhydride (PAH) (analytical reagent, ≥97.0%), and sodium acetate, trihydrate (CH3COONa·3H2O) (analytical reagent, ≥99.5%) were purchased from Sigma-Aldrich. 1,2-Dichloroethane (DCE) (analytical reagent, ≥99.5%), sodium hydroxide (NaOH) (analytical reagent), methanol (CH3OH) (analytical reagent, ≥99.5%), phenolphthalein, and ethanol (C2H5OH) (analytical reagent, ≥99.5%) were supplied by Sinopharm Chemical Reagents Co., Ltd., China. A concentrated sulfuric acid (H2SO4) (95‒98 wt%) was obtained from Xinyang City Chemical Reagents Plant, China. Potassium biphthalate (≥99.95%) was purchased from Tianjin City Chemical Reagents Institute Co., Ltd., China. Chloroform-d (CDCl3) (≥99.8%), methanol-d4 (CD3OD) (≥99.8%), and potassium bromide (KBr) (specpure reagent) were supplied by Aladdin Industrial Corp., China. Distilled water was home made in our laboratory using a stainless-steel water distiller. The PS was purified by reprecipitation into a large amount of CH3OH from DCE. Other chemicals were used as received without further purification.

Synthesis of An Na-Salt Sulfonated PS Ionomer

Purification of the PS. An amount of the PS was stirred and well dissolved in DCE at room temperature (RT) (i.e., ~25 °C) to form a solution of ~0.1 g mL⁻¹, which was then injected with a syringe into a large amount of CH3OH (i.e., ~20 times the volume of the solution) to precipitate a white fibrous product. On standing overnight in a refrigerator (i.e., at ~5 °C), the product was sequentially Buchner-filtered off, washed with CH3OH at least 3 times, air-dried in a fume hood overnight, and finally dried in vacuo at 70 °C for at least 24 h.

Sulfonation of the PS. The purified PS was solution sulfonated with propionyl hydrogen sulfate (PHS), which was prepared in situ from solution reaction of the c-H2SO4 with PAH (Equations S1 and S2). Based on assumptions that both the H2SO4-PAH and PS-PHS reactions were 100% complete and that a single –SO3H group was grafted to the para-C of the benzene ring in each sulfonated repeat-unit of the PS, the required amount of the c-H2SO4 against the PS was determined according to a PS theoretical degree of sulfonation (DS) of 25 mol%.

The PAH amount was hence equal to the mole number of the H2SO4 molecules to ensure that PHS was primarily produced from the H2SO4-PAH reaction.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{C}^\text{O}\text{C}\text{CH}_2\text{CH}_3 + \text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{C}^\text{O}\text{SO}\text{OH} + \text{CH}_2\text{CH}_2\text{C}^\text{O}\text{OH}
\end{align*}
\] (S1)
Under these circumstances, a predetermined amount (g) of the purified PS was stirred and well dissolved in DCE in a three-necked flask to form a solution of ~0.1 g mL⁻¹. Meanwhile, a thus specified amount (mL) of PAH was stirred with DCE under N₂ atmosphere in a Claisen flask immersed in ice water bath to form a solution of ~6.0 × 10⁻³ mL mL⁻¹, into which an accordingly quantified amount (mL) of the c-H₂SO₄ was then pipetted dropwise and further reacted with PAH for 1 h to produce PHS in a DCE solution. The PHS solution, as the sulfonylating agent, was immediately transferred into a pressure-equilibrating dropping funnel fitted to the three-necked flask, and dropped slowly (1 drop/3–6 s) into the vigorously stirred PS solution under N₂ atmosphere. The PS–PHS reaction system was refluxed at a water-bath temperature of ~50 °C for 4 h (including the dropping time), when a small amount of CH₃OH (~1.0% the DCE volume used to dissolve the PS amount) was pipetted in to react for 0.5 h, thus terminating the sulfonylation reaction. The reacted solution was immediately injected with a syringe into a large amount of boiling distilled water (~20 times the solution volume) to precipitate a white flocculent product, i.e., sulfonylated PS (SPS), floating on the surface. On standing at RT overnight, the SPS product was sequentially Buchner-filtered off, immersion-washed with distilled water at least 3 times, air-dried in a fume hood overnight, vacuum-dried at 70 °C for 2 days and finally at 100 °C for at least 4 days.

**Determination of the SPS Degree of Sulfonylation by Acid–Base Titration.** A CH₃OH solution of an accurately weighed mass of the well-dried SPS (~1.0 × 10⁻² g mL⁻¹) was titrated in an Erlenmeyer flask against an NaOH CH₃OH solution from a basic burette, which, with a nominal concentration of 5.0 × 10⁻² M, was in turn titrated *in situ* to evaluate its effective concentration with a precise amount of potassium-biphthalate standard of ~1.0 × 10⁻² g mL⁻¹ in distilled water in another Erlenmeyer flask. For both the titrations, a phenolphthalein indicator solution in an ethanol/water (19/1 v/v) mixed solvent (~1.0 × 10⁻² g mL⁻¹) was used to identify the first occurrence of a reddish colour as the equivalence point. The actual DS of the SPS was therefore calculated using the following equation,

\[
DS = \frac{cV}{cV + \frac{m - M_cF}{M}} \times 100% \tag{S3}
\]

where m is the accurately weighed mass (g) of the well-dried SPS, c the effective molar concentration (mol L⁻¹, or M) of the NaOH CH₃OH solution, V the volume (L) of the NaOH CH₃OH solution consumed until the equivalence point of the SPS CH₃OH solution titration, M and Mᵣ the molar masses (g mol⁻¹) of unsulfonated and sulfonated styrene units (i.e., 104.16 and 184.26), respectively. To minimize any uncertainty of the result, the median DS value from five parallel titrations was taken as the DS of the SPS synthesized.

**Salinization of the SPS with Na⁺ Ions.** With an initial intent to ensure complete conversion of the –SO₂H to –SO₃Na groups during the salinization (Equation S4), if possible, the mole ratio of the SPS –SO₂H groups to Na⁺ ions was delicately controlled at 1/1.05. That is, the amount of CH₃COONa·3H₂O employed was 5% in excess of its stoichiometric amount (mol) equal to the –SO₃Na content (mol) (i.e., cV in Equation S3) actually present in a certain mass (i.e., m in Equation S3) of the SPS (with its DS determined above from Equation S3) used. Therefore, an amount of the SPS was stirred and well dissolved in CH₃OH to form a clear solution of ~2.0 × 10⁻² g mL⁻¹, into which a hence specified amount of CH₃COONa·3H₂O, in the form of a CH₃OH solution of still ~2.0 × 10⁻² g mL⁻¹, was pipetted dropwise. The reaction solution was then allowed to be stirred at RT for 24 h, from which the contained CH₃OH solvent was subsequently removed by rotary evaporation at 45 °C to precipitate a white product. The product was dissolved in a large amount of boiling distilled water overnight, Buchner-filtered off and then immersion-washed again with distilled water at least 3 times to thoroughly remove any remaining CH₃COONa present in it. Finally, the neat product, i.e., Na-salt SPS ionomer (SPS–Na), was air-dried in a fume hood overnight, vacuum-dried at 70 °C for 2 days and further at 100 °C for at least 3 days.

**¹H nuclear Magnetic Resonance (NMR) Spectroscopy**

To verify that the PS sulfonylation was successful, an NMR spectrometer (Bruker, Ascend™ 600 MHz) was employed to collect the ¹H solution-state NMR spectra of the SPS and SPS–Na against that of the (purified) PS at 600 MHz with respect to a tetramethylsilane internal standard. For the runs, small amounts (5–10 mg) of the PS, SPS, and SPS–Na, on vacuum drying at 100 °C for at least 24 h, were well dissolved in 1.0 mL of CDCl₃, CD₂OD, and CD₃OD, respectively, in an NMR tube to form a uniform solution sample of ~5–10 mg mL⁻¹. In the spectra of all the three solution samples, the assignments of the ¹H-peaks chemical-shift (δ) values were analyzed with reference to the literature (Ref. 29 and 30 in the lett.) plus with the aid of ChemDraw simulation.
Fourier Transform Infrared (FTIR) Spectroscopy

To further verify the success in the PS sulfonation, the FTIR absorption spectra of the SPS and SPS–Na were measured against that of the (purified) PS in a small mid-IR range of 1300–900 cm\(^{-1}\). An FTIR spectrometer (Thermo Fisher, Nicolet 670) was used to collect the absorption spectra of a 4 cm\(^{-1}\) resolution under N\(_2\) atmosphere based on 32 scans in the transmission mode. For the runs, the samples were prepared as KBr pellets by grinding together, using a pestle and mortar, ~0.5 mg of each of the three polymer powders and ~50 mg of KBr dried with an infrared baking lamp followed by RT compression molding of the mixture powder on a hydraulic press. In the spectra of the three pellet samples, the assignments of the characteristic vibrational-absorption peaks were analyzed with reference to the literature (Ref. 31 in the lett.).

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

To prove that the SPS salinization was successful and, more quantitatively, evaluate the degree of neutralization (DN) of the SPS–Na, an ICP-OES instrument (Agilent, ICP-OES 730) was employed to measure the Na content (g g\(^{-1}\)) of the SPS–Na against those of the (purified) PS and SPS. Digestion of the three polymers was first conducted as follows. A mass (~0.1 g) of the PS, SPS, and SPS–Na was accurately weighed into a 50-mL Teflon\(^9\) digestion tube, into which a mixture of ~5 mL of concentrated nitric acid, ~1 mL of hydrochloric acid and ~1 mL of hydrofluoric acid was then added. The tube was subsequently capped and placed in a stainless-steel reactor, which further stood in an oven at 200°C for ~5 h and was finally air-cooled to RT. Measurement of the three polymers was therefore made according to the following. The cooled solution in the tube was transferred into a 25-mL volumetric flask, into which distilled water was then added until the constant volume. The stopped flask was subsequently allowed to tumble and hence stand still overnight for the solution homogenization. Finally, the solution sample was measured by the ICP-OES instrument against (the calibration curve of) the standard Na\(^+\) aqueous solution. For the SPS–Na, the DN was evaluated from the Na content by means of the equation,

\[
DN = \frac{c_{Na}[M + DS(M_s - M)]}{DS[M_{Na} - c_{Na}(M_s - M_s)]} \times 100\% 
\]  

(S5)

where DS is the SPS degree of sulfonation evaluated experimentally from Equation S3, M, M\(_s\), and M\(_{Na}\) the molar masses (g mol\(^{-1}\)) of styrene, sulfonated styrene, and Na\(^+\)-neutralized sulfonated styrene units (i.e., 104.16, 184.26, and 206.25), respectively, M\(_{Na}\) the molar mass (g mol\(^{-1}\)) of Na (i.e., 22.99), and c\(_{Na}\) the Na content (g g\(^{-1}\)) of the SPS–Na measured by ICP-OES.

Small-Angle X-Ray Scattering (SAXS)

To ascertain if the –SO\(_4^−\)–Na\(^+\) ion pairs were self-assembled into ionic aggregates in the SPS–Na, the SAXS profile from the SPS–Na, against that from the (purified) PS, was collected using the SAXS module of an X-ray diffractometer (PANalytical, Empyrean) having a rotating anode X-ray generator equipped with a graphite monochromator (Cu Kα; λ = 1.5406 Å) operating at 40 kV and 60 mA. For the runs, an amount (~0.1 g) of each of the PS and SPS–Na was fully ground with a pestle and mortar into a fine powder, which was then evenly spread over a silicon-substrate sample holder for SAXS scan in the reflection mode at RT. The scans were conducted across scattering angles (2θ°) of 0.5–5.0° at a rate of 0.225 ° min\(^{-1}\).

High-resolution Transmission Electron Microscopy (HR-TEM)

A high-resolution transmission electron microscope (JEOL, JEM-2100) with point and lattice resolutions of 0.23 and 0.14 nm, respectively, was employed at an acceleration voltage of 200 kV to observe the morphology of the –SO\(_4^−\)–Na\(^+\) ionic aggregates of the synthesized SPS–Na well vacuum-dried at 100°C for at least 3 days and then physically aged at RT in vacuo for 2 weeks. A small amount (≤5.0 mg) of the aged, supposedly anhydrous SPS–Na was fully ground with an agate pestle and mortar into a fine powder of ~1 μm in diameter, which was then sonicated in anhydrous C\(_2\)H\(_2\)OH for 10–15 min as necessary for its visually uniform dispersion. A drop of the supernatant of the sonicate was subsequently pipetted onto a lacey carbon film supported on a 200-mesh copper grid and dried thoroughly with an infrared baking lamp. The prepared sample was finally subjected to TEM observation under different magnifications: a representative TEM image was taken under such a magnification that the field of view encompassed 80–90 aggregates; other images were taken under higher magnifications.

Wide-Angle X-Ray Scattering (WAXS)

The WAXS pattern of the SPS–Na aged at RT in vacuo for 2 weeks, against that of the (purified) PS, was collected by use of an X-ray diffractometer (PANalytical, Empyrean) having a rotating anode X-ray generator equipped with a graphite monochromator (Cu Kα; λ = 1.5406 Å) operating at 40 kV and 60 mA. The scattered X-ray was received by a PiXcel\(^{3D}\) detector. For the runs, an amount (~0.1 g) of each of the PS and aged SPS–Na was fully ground with a pestle and mortar into a fine powder, which was then evenly spread onto a silicon-substrate sample holder for WAXS scan in the reflection mode at RT. The scans were performed over 2θ° of 5–60° at a rate of 1 ° min\(^{-1}\).

The aged SPS–Na was assumed to be primarily a two-phase system of nm-sized –SO\(_4^−\)–Na\(^+\) ionic aggregates dispersed in PS matrix. Based on this, the WAXS pattern of the ionic aggregates was resolved by a weighted subtraction of the WAXS signal of the PS from that of the aged SPS–Na as described by

\[
I_s(2θ) = I_s(2θ) - fI_r(2θ) 
\]  

(S6)

where \(I_s(2θ)\) and \(I_r(2θ)\), and \(I_f(2θ)\), respectively, are the scattered X-ray intensities from the PS (reference), aged SPS–Na (sample), and ionic aggregates at a given 2θ, and f an adjustable scale factor which considers the differences in electron-density and thickness between the sample and reference. The f was determined by a trial-and-error method based on, upon the subtraction, full suppression of the “amorphous” peaks of the PS matrix combined with leveling-off of the declining baseline in the resolved WAXS pattern.

Provided that the WAXS pattern resolved of the ionic aggregates displayed Bragg-type reflection(s), the average diameter, D, of the crystallites (if spherical) within the ionic aggregates was then estimated using Scherrer’s equation,
where \( k \) is an empirical shape factor (here \( 0.90 \) taken for the ionic aggregates), \( \lambda \) the wavelength of the X-ray (1.5406 Å), \( B \) the full width at half height (FWHH) of a major WAXS peak, and \( \theta \) a half of the \( 2\theta \) of the major peak. Also, an interplanar (i.e., Bragg) spacing \( (d) \), i.e., separation between two neighboring, parallel crystallographic planes of the aggregate crystallites, was calculated by Bragg’s law,

\[
d = \frac{\lambda}{2 \sin \theta}
\]

where \( \lambda \) and \( \theta \) have the same physical senses as those in Equation S7.

In addition, according to the experimental procedure described in Paragraph 1 of this section, the WAXS patterns of CH\(_3\)COONa•3H\(_2\)O and CH\(_4\)COONa prepared by dehydration of CH\(_3\)COONa•3H\(_2\)O at 180 °C in vacuo for 3 h were collected as well, with which the WAXS pattern of the –SO\(_3\)–Na\(^+\) ionic aggregates of the aged SPS–Na was compared.

### Differential Scanning Calorimetry (DSC)

A differential scanning calorimeter (Perkin Elmer, DSC 8000) was employed to examine any thermal transition(s) of the SPS–Na samples physically aged at RT in vacuo for increasing durations (0 h, 3 days, 2 weeks, and 3 months) under an N\(_2\) atmosphere of 20 mL min\(^{-1}\). Prior to the measurements, the instrument was calibrated in both temperature and heat flow with indium and zinc standards. For the runs, small amounts (3–5 mg) of the well-dried as-synthesized SPS–Na, preferably in pellet form, each were encapsulated with an aluminium lid into a cylindrical, flat-bottomed aluminium pan, which was then enclosed in the DSC sample cell against an empty (i.e., sample-free) aluminium pan–lid capsule in the reference cell.

To prepare and run the 0 h aged (i.e., unaged) sample, the cells were heated from RT to 260 °C to minimize any effect(s) of sample preparation history, then cooled to \( -30 \) °C, both at a rate of 10 °C min\(^{-1}\), and finally, immediately, heated again to 350 °C at a rate of 40 °C min\(^{-1}\); its corresponding baseline was collected by running the same heating–cooling–heating consecutive cycles of the cells both enclosing an empty pan–lid capsule. The aged samples were prepared and run similarly except that, upon the cooling cycle, they were aged at RT in a vacuum oven (i.e., under strictly anhydrous conditions) for the predetermined times, and then replaced into the DSC sample cell for the second heating cycle starting from \( -30 \) °C; accordingly, their baseline was collected only by running the same (second) heating cycle of the cells.

For all the samples, the DSC traces were recorded in the second heating cycle, from which sample-mass normalized, baseline-subtracted heat flow (W g\(^{-1}\)) was plotted against temperature (°C) to constitute the DSC thermograms for analysis. In each thermogram, the inflection point (°C) of any step was read as a glass transition temperature (\( T_g \)), the peak-point (°C) and area (J g\(^{-1}\)) across any peak were taken as the temperature and enthalpy (or intensity) of an endotherm (or exotherm), respectively.

### High-Temperature Wide-Angle X-Ray Scattering (HT-WAXS)

If a notable endotherm occurred during the above DSC experiments for the SPS–Na aged at RT in vacuo for 3 months, then its WAXS patterns, against those of the (purified) PS, were collected at RT (before the endotherm onset) and a high temperature (after the endotherm completion) with an X-ray diffractometer (Bruker, D8 Discover) having a rotating anode X-ray generator equipped with a graphite monochromator (Cu K\(_\alpha\); \( \lambda = 1.5406 \) Å) operating at 40 kV and 40 mA. The scattered X-ray was received by a LynxEye detector fitted with receiving and divergence slits of 1 and 8 mm, respectively.

For the runs, an amount (~0.5 g) of each of the PS and aged SPS–Na was finely ground with a pestle and mortar into a fine powder, which was then evenly spread onto a sample stage for WAXS scan in the reflection mode. The scan was conducted across 20’s of 5–60° at a rate of 1° min\(^{-1}\). The aged SPS–Na sample, in the relatively large amount of ~0.5 g, had to be prepared differently from those for DSC but similarly to that for TEM and RT-WAXS, that is, the SPS–Na was aged at RT in vacuo for 3 months immediately following (the 100 °C vacuum drying at the end of) its synthesis without prior subjection to high temperatures in the DSC cell. Either of the two samples was first WAXS-scanned on the sample stage at RT, and then at the predetermined high temperature after the stage, under a compressed air atmosphere, was heated to that temperature at a rate of 20 °C min\(^{-1}\) and annealed there for ~5 min.

At each of the temperatures, the WAXS pattern of the aged SPS–Na’s ionic aggregates was therefore resolved likewise by a weighted subtraction described by Equation S6, in which the \( f \) was estimated using a similar trial-and-error method. The pattern of the aggregates at RT was finally compared with that at the high temperature to check if there was any structural change(s) within the aggregates across the endotherm transition of the aged SPS–Na.