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

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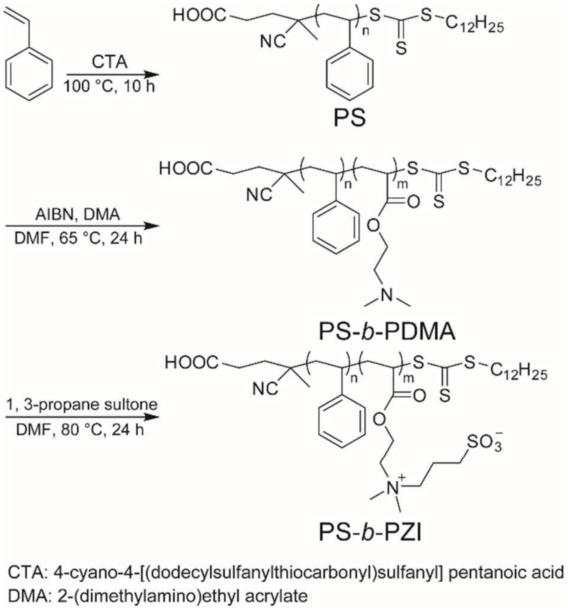
We have prepared poly(ammonium-based zwitterion) block copolymers forming nanosegregated assemblies. Incorporation of lithium bis(trifluoromethanesulfonyl)imide ($LiTf_2N$) into the assemblies, setting up ionic liquid-like ion pairs of the ammonium cations and Tf_2N anions, endowed the polyzwitterion domains with ion transporting ability.

Ionic liquids are rapidly emerging as neoteric liquid materials to traditional electrolytes, because of their remarkable combination of properties including negligible vapour pressure, flame retardancy and high ionic conductivity.[1] In the last 20 years a number of novel ionic liquids have been designed that further improve electrolyte performance.[2,3] The '*nanostructurisation*' of ionic liquids is one strategy to do this, enabling the allocation of incompatible functions and/or properties onto different nanodomains in the resulting ionic liquid.[4] In particular, ionic liquids are now being used as one component of block copolymers forming nanostructured assemblies. This approach is expected to yield nanostructured polyelectrolytes having high ionic conductivity, due to the low glass transition temperature (T_g) of ionic liquids, and also good mechanical stability deriving from the other component.[5] Another strategy is '*zwitterionisation*' of ionic liquids, meaning the tethering of the cation and anion of ionic liquids through covalent bonds. We have previously found that some imidazolium-, ammonium- and phosphonium-based zwitterions are capable of forming a homogeneous complex with some lithium salts or acids, giving a liquid medium with a low T_g.[6] This is believed to be due to the formation of ionic liquid-like ion pairs between the cation of zwitterions and the anion of the added salts or acids. The resulting liquid medium acts as an ion active matrix, transporting lithium cation or proton selectively, because zwitterions themselves never respond to potential gradient as their ion structures have no net charge.[7] According to these studies of ionic liquid-based electrolyte design, a marriage between the two strategies of '*nanostructurisation*' and '*zwitterionisation*' would be one of potential strategies to generate ideal solid polyelectrolytes. In the present study, we designed and synthesised poly(styrene-*b*-ammonium-based zwitterion) block copolymers as a basic design and investigated their applicability as polyelectrolytes.

Our block copolymers, PS-*b*-PZI-*x* (The index *x* is the mol % of zwitterion unit in the block copolymer), were synthesised by the following procedure (Scheme 1). A polystyrene-*b*-poly(2-(dimethylamino)ethyl acrylate) (PS-*b*-PDMA-*x* were synthesised by reversible addition-fragmentation chain



Scheme 1 Synthesis of PS-*b*-PZI.

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transfer polymerisation, according to the literature.[8] Three types of PS-*b*-PDMA-*x* were prepared: PS-*b*-PDMA-19.7 (M_n: 16.4 kg・mol^{-1}), PS-*b*-PDMA-44.1 (M_n: 6.64 kg・mol^{-1}) and PS-*b*-PDMA-64.3 (M_n: 10.8 kg・mol^{-1}). PS-*b*-PDMA-19.7 was synthesised by elongation of DMA monomer from PS (M_n = 12.4 kg・mol^{-1}) and the others were synthesised from PS (M_n = 3.39 kg・mol^{-1}). The number average molecular weight was determined by ^{1}H NMR measurement, and M_n for the initial PS was determined by SEC measurement (See ESI). A subsequent quaternisation reaction of the amine groups of these three types of PS-*b*-PDMA-*x* with 1, 3-propanesultone gave polystyrene-*b*-poly(2-(dimethyl-(3-sulfopropyl)-ammonium betaine)ethyl acrylate) (PS-*b*-PZI-*x*) block copolymers. By comparing the ^{1}H NMR spectra of PS-*b*-PDMA-64.3 and PS-*b*-PZI-64.3, we found that the quaternisation reaction of the amine groups into zwitterion groups proceeded quantitatively. The molecular characteristics for PS-*b*-PZI-*x* were not examined because this family was slightly soluble in conventional solvents. This is because the molecule comprises two segments having opposite polarity. Details of the synthesis of these polymers are described in †ESI.

Upon looking at the solubility of PS-*b*-PZI-64.3 in conventional solvents, we found that it showed dispersion behaviour in H_2O. To examine the dispersion mechanism, we performed ^{1}H NMR measurement for PS-*b*-PZI-64.3 in D_2O. In the ^{1}H NMR spectrum of PS-*b*-PZI-64.3 in D_2O (Fig. 1(a)), no signals corresponding to PS block were observed, indicating that PS-*b*-PZI-64.3 formed micelles with PS core and PZI shell in D_2O. It is well known that block copolymers form core-shell micelles in selective solvents for one of their blocks. Comparing the dispersion behaviour of PS-*b*-PZI-64.3 with that of the other PS-*b*-PZI-*x*, it was found that the dispersibility of PS-*b*-PZI-*x* decreased as the decrease of the PZI composition.

If the condensation of dispersed solutions of PS-*b*-PZI-*x* in co-existence with lithium salts proceeds by forming and retaining ion pairs between the PZI segments and lithium salts, then we expect a nanosegregated matrix to be formed in which PS cores form dispersed globular domains surrounded by a continuous ionic liquid-like domain composed of the PZI segments and lithium salts. Considering the dispersion behaviour of a series of PS-*b*-PZI-*x* in H_2O, we concluded that PS-*b*-PZI-64.3 was the most suitable for preparing homogeneous nanostructured assemblies among the obtained block copolymers. We accordingly prepared a solution of PS-*b*-PZI-64.3 with an equimolar amount of lithium bis(trifluoromethanesulfonyl)imide ($LiTf_2N$) per ZI unit in H_2O (7% w/w), and cast it onto a substrate using a pipette. Slow evaporation of the solvent at 70 °C followed by vacuum drying for 4 hours at 70 °C resulted in the formation of a film-state sample (PS-*b*-PZI-64.3/$LiTf_2N$ film). The morphology of this film was investigated by transmission electron microscopy (TEM) and by making small angle X-ray scattering (SAXS) measurements. In the SAXS pattern a single broad peak was observed at small angles, suggesting the formation of randomly aggregated micelles (See ESI). TEM results provided further evidence that the micelle structures were maintained beyond the condensation process. TEM measurements were carried out on PS-*b*-PZI-64.3/$LiTf_2N$ film after the PS domains had been stained with OsO_4, and the film was sliced into sections of thickness approximately 70 nm using a glass knife. Fig. 1(b) shows a TEM image for PS-*b*-PZI-64.3/$LiTf_2N$ film. The PS segments form globular domains having a diameter of about 9 nm in the film. Assuming that the radius and density of the PS globular domains are 4.5 nm and 1.05 g・mol^{-1}, the number of PS-*b*-PZI-64.3 polymer chains forming a core-shell micelle is estimated to be about 80.

To determine whether the PZI segments, that form a complex with $LiTf_2N$, set up ionic liquid-like domains around the PS core domains in the condensed state, we undertook DSC measurement on the film (See ESI). Upon heating, a glass transition behaviour was observed at 122 °C for PS-*b*-PZI-64.3, whereas for PS-*b*-PZI-64.3/$LiTf_2N$ film, T_g = 78 °C. We attribute this decrease in T_g to the formation of ionic liquid-like ion pairs between the ammonium cation of the PZI segments and the Tf_2N anion of added $LiTf_2N$, through the hard and soft, acids and bases principle. To gain further insight, we prepared PZI-homopolymer and examined its thermal behaviour in the presence and absence of $LiTf_2N$. As well as PS-*b*-PZI-64.3, PZI-homopolymer underwent a decrease of T_g upon the addition of $LiTf_2N$, from 150 °C to 83 °C, which was approximately the same temperature as T_g for PS-*b*-PZI-64.3/$LiTf_2N$ film. From these comparisons we conclude that condensation of the polyzwitterion block copolymer and lithium salts causes the

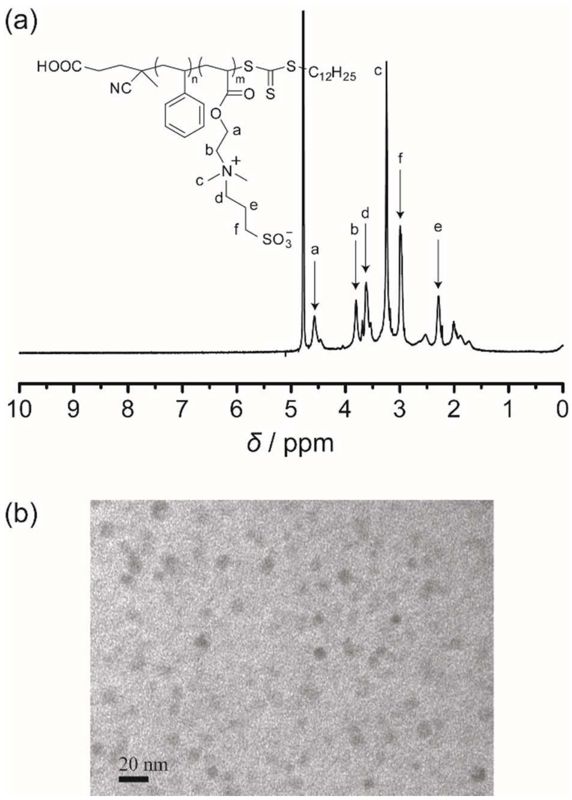

Fig. 1 (a) ^{1}H NMR spectrum of PS-*b*-PZI-64.3 in D_2O and (b) TEM image of PS-*b*-PZI-64.3/$LiTf_2N$ film. PS domains were darkened by OsO_4 staining.

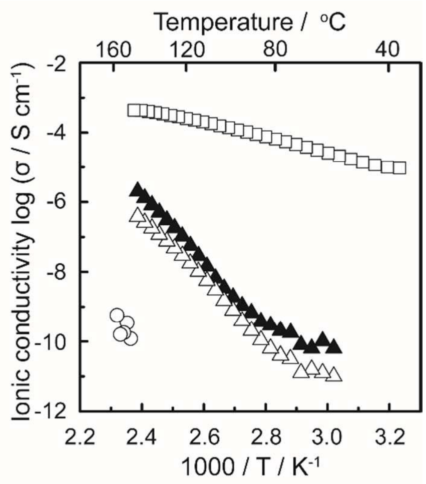

Fig. 2 Ionic conductivities of PS-*b*-PZI-64.3 film (○), PS-*b*-PZI-64.3/LiTf$_2$N film (△), PZI-homopolymer/LiTf$_2$N film (▲) and PS-*b*-PZI-64.3/phosphoric acid film (□) on heating.

formation of nanosegregated matrix consisting of PS core and ionic liquid-like shell domains.

The ionic conductivities of the resulting films were measured over a range of temperatures. The obtained samples were thermally stable in the measurement temperature range, which was confirmed by TG/DTA measurement (See ESI). Fig. 2 shows Arrhenius plots of the conductivities as a function of temperature. The ionic conductivity of PS-*b*-PZI-64.3 film was very low, and was under below the detection limit of our system at temperatures less than about 150 °C. In contrast, ion conduction behaviour was observed very clearly with PS-*b*-PZI-64.3/LiTf$_2$N film. As an example, the ionic conductivity of PS-*b*-PZI-64.3 film was 1.2 $\times 10^{-10}$ S cm^{-1} at 150 °C, and that of PS-*b*-PZI-64.3/LiTf$_2$N film was 3.8 $\times 10^{-7}$ S cm^{-1} at 146 °C. These results support our conclusion that the PZI segments preferentially interact with LiTf$_2$N and set up an ionic liquid-like environment in the nanostructured film. For comparison, we also measured the ionic conductivity of PZI-homopolymer/LiTf$_2$N film. Although the ionic conductivity of PS-*b*-PZI-64.3/LiTf$_2$N film was slightly lower than that of PZI-homopolymer/LiTf$_2$N film, the activation energies of these two films were similar over a broad range of temperature. For example, the activation energies of PS-*b*-PZI-64.3/LiTf$_2$N film and PZI-homopolymer/LiTf$_2$N at temperatures between 80 °C and 120 °C are calculated to be 184 and 173 kJ mol^{-1}, respectively. These results suggest that the PS core domains are located in the nanostructured film without preventing the PZI/LiTf$_2$N shell domains from forming a macroscopically continuous ion conductive pathway. There are a number of pioneering works that report on nanostructured electrolytes for lithium ion conduction.[9] They have provided diverse insights that are significant for the development of new energy devices. The obtained results show potential utility of polyzwitterion as building blocks for the design of nanostructured electrolytes.

Recently, zwitterions have been studied for the development of proton conductive materials because of their ability to dissociate acids.[10] We expected that combination of PS-*b*-PZI-64.3 and acids would lead to the construction of nanostructured matrix for proton conduction. As an acid, phosphoric acid was selected because it possesses thermal stability in the wide range of temperatures. We have prepared PS-*b*-PZI-64.3/phosphoric acid film by a similar procedure and studied its ion conduction behaviour. The ionic conductivity of PS-*b*-PZI-64.3/phosphoric acid film was 9.9 $\times 10^{-6}$ S cm^{-1} at 40 °C, which increased linearly as elevating temperature until 150 °C with activation energy of 40 kJ mol^{-1}, indicating that the PZI segments enhanced the proton dissociation of phosphoric acid. Comparing with PS-*b*-PZI-64.3/LiTf$_2$N film, PS-*b*-PZI-64.3/phosphoric acid film had greater ionic conductivity and lower activation energy. These differences can be explained by assuming that ion conductive property of PS-*b*-PZI-64.3/LiTf$_2$N film is dominated by the vehicle mechanism while that of PS-*b*-PZI-64.3/phosphoric acid film is based both on vehicle and hopping (Grotthuss) mechanism[11] *via* hydrogen bonding network of bound water molecules which remain around PZI segments even after vacuum drying and heating processes. Zwitterionic compounds are known to bind water molecules strongly *via* electrostatically induced hydration.[12] Taking all of these results into account, we believe that polyzwitterion block copolymer systems are well suited as nanostructured polyelectrolytes capable of transporting lithium ions and protons via the appropriate choice of species added.

In conclusion, we have demonstrated that the aggregation of core-shell micelles formed by poly(styrene-*b*-ammonium-based zwitterion) block copolymer results in the formation of nanostructured ion active polymer films. By preparing films in the co-existence with a lithium salt, the resulting polymer films acquire ion conductive properties, which is due to the ability of polyzwitterion segments to form an ionic liquid-like environment with lithium salts. Furthermore, the process of film formation with an acid provides a proton conductive matrix owing to the ability of polyzwitterion segments to facilitate proton dissociation of acids. We believe that the design of ionic liquids by combining '*nanostructurisation*' and '*zwitterionisation*' as in the present study provides a stepping stone for the development of ideal solid polyelectrolytes suitable for use in diverse battery systems.

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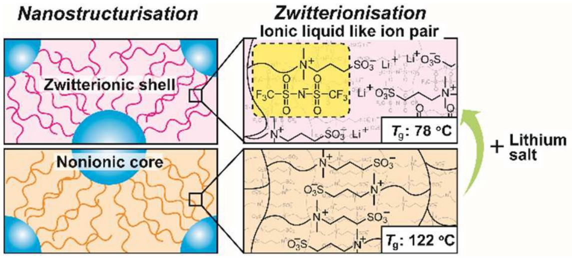
Graphical abstract



Textual abstract

We have designed nanostructured polyelectrolytes through the co-aggregation of micelles bearing polyzwitterion and lithium salts.