MULTI-LENGTH SCALE STRUCTURE OF SEGMENTED PEG-BASED IONOMERS

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Introduction

Polymeric solid electrolytes have been subject of intensive research for potential applications in electrochemical devices, especially lithium-ion batteries. The most widely studied system is based on poly(ethylene glycol) (PEG), which can effectively solvate a variety of alkali and alkaline cations.[1] Although mixtures of polymers with salts show reasonable conductivity at room temperature,[2] they suffer from the undesirable electrode polarization due to anion aggregation at the cathode surface.[3] Single-ion conductors with anions fixed to polymer backbone are able to resolve this problem and achieve a cation transference number of 1.[1] Unfortunately, the single-ion conductors studied to date show far lower conductivity than the bi-ion conductor. Understanding the structure and cation transport mechanism in single-ion conductors is critical for designing future cation transport materials with high conductivity.

In this study, the structure and ionic association behavior of PEG-based ionomers are investigated as a function of PEG segment length, cation type, and temperature. A series of sulfonated polyester ionomers with well-defined PEG spacer lengths are synthesized by melt polycondensation. Multiple-angle X-ray scattering data reveal the morphology of the ionomers at different length scales. The effects of temperature on the nanoscale structures of these ionomers are investigated by in situ X-ray scattering over a wide temperature range.

Experimental

PEG-based ionomers were prepared by a two-step catalyzed melt transesterification of PEG oligomer diol with a mixture of Dimethyl 5-sulfoisophthalate sodium salt and dimethyl isophthalate to give random ionomers of varying ion content. The molecular weight of PEG spacer was 400, 600, 900, or 3000, and the cation was exchanged from sodium to cesium by dialysis. The concentrated ionomer solutions were freeze-dried after diafiltration and then vacuum-dried at 120 ^{o}C to constant mass. The ionomers are denoted as PEGx-yM, where x is the molecular weight of PEG oligomer, y is the percent of sulfonated phthalates over total amount of phthalates in ionomers, and M represents the type of cation (Na or Cs). PEG600-

50% Na designates the ionomers with PEG spacer length of 600 g/mol and 50% sulfonated phthalates. Note that y is not the neutralization level of the acid and theoretically all the acids in different ionomers are neutralized with metal cations.

The multi-angle X-ray scattering system (MAXS) used Cu X-ray from a Nonius FR 591 rotating-anode generator operated at 40 kV and 85 mA. The bright, highly collimated beam was obtained via Osmic Max-Flux optics and pin collimation in an integral vacuum system. The scattering data were collected using a Bruker Hi-Star multiwire detector with a sample to detector distance of 11, 54 and 150 cm. Temperature scanning was performed from room temperature to 150 ^{o}C with a step size of 25 ^{o}C and a heating rate of 10 ^{o}C/min. The ionomers were then cooled back down to room temperature at cooling rate of 10^{o}C/min. The samples were held at each temperature for 10 min before starting the X-ray data collection. The 2-D data reduction and analysis were performed using Datasqueeze software.[4]

Results and Discussion

Figure 1 shows the room temperature X-ray scattering results for five fully sulfonated PEG-based ionomers over a wide range of scattering angle (q = 0.1 to 18 nm^{-1}). The morphological features observed in the X-ray scattering data of these ionomers are summarized in Table 1. The ionomers are amorphous when the PEG spacer length is short (400 or 600 g/mol). As the PEG segment length increases to 900 or 3000 g/mol, the polymer chain starts to crystallize. The crystallinity of fully sulfonated polyester ionomers based on PEG length of 900 g/mol is highly dependent on the thermal history, while the fully sulfonated polyester ionomer based on PEG with M = 3000 g/mol is always semi-crystalline. The crystalline reflection peaks at 13.6 nm^{-1}, 16.5 nm^{-1} and 18.5 nm^{-1} correspond well to the main crystalline reflections of typical PEO crystals having a helical chain conformation and a monoclinic lattice.[5] Because the lattice parameter remains unchanged in the PEG-based ionomers, we conclude that the ions are excluded into the amorphous phase. When the counterion is sodium, there is no "ionomer peak" in the expected angular range at room temperature. In contrast, when the cation is exchanged from sodium to a higher atomic number species such as cesium, a broad peak appears at ~7 nm^{-1}. The origin of this peak is not well-understood. The angular position of the peak is much higher than the typical ionomer peaks observed in various ionomer systems (1-5 nm^{-1}) and it is also much broader than typical ionomer peaks. Small-angle X-ray scattering shows the usual ionomer upturn at low q (roughly with intensity scaling as q^{-2}) for all of the ionomers. The semi-crystalline ionomers (with PEG M ≥ 900) also show three small angle peaks superimposed on this power law. The peak positions relative to the first peak position are 1:2:3, which might indicate a layered structure. Typical semicrystalline polymers usually show only one crystalline lamellae-lamellae scattering peak due to a lack of ordering and the limited contrast between the amorphous and crystalline domains. In these semicrystalline PEG-based ionomers, the existence of multiple scattering peaks is probably the result of higher contrast between the crystalline domains from which the cations are excluded and the amorphous domains containing the cations. For example, although PEG900 – 100% Cs has less crystallinity shown in the wide-angle regime, the small-angle scattering peaks are sharper than PEG3000 – 100% Na, because the higher atomic number cation Cs^+ enhances the amorphous/crystalline contrast relative to the lower atomic number cation Na^+.

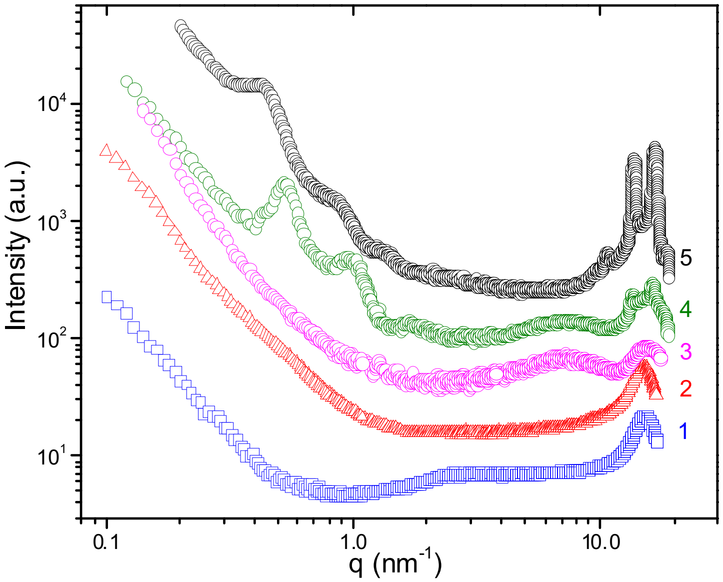

Figure 1. X-ray scattering intensity vs. scattering vector q for fully sulfonated PEG-based ionomers neutralized by monovalent cations. Log-log scale is used. Sample numbers correspond to materials listed in Table 1.

Table 1. Morphological features observed in X-ray scattering of PEG-based ionomers.

Sample	**Materials**	**q<2 nm^{-1}**	**2<q<10 nm^{-1}**	**q>10 nm^{-1}**
1	PEG400 – 100% Na	Upturn	No Peak	Amorphous
2	PEG600 – 100% Na	Upturn	No Peak	Amorphous
3	PEG600 – 100% Cs	Upturn	Broad Peak at 7 nm^{-1}	Amorphous
4	PEG900 – 100% Cs	Upturn & three scattering peaks	Broad Peak at 7 nm^{-1}	Semicrystalline
5	PEG3000 – 100% Na	Upturn & three scattering peaks	No Peak	Semicrystalline

To further understand the morphology in our ionomers systems, *in situ* X-ray scattering was performed over a wide temperature range to investigate the effects of temperature on the crystallinity and ionic association behavior. High-temperature X-ray scattering on the sodium salt of the fully sulfonated reveals a new peak in the angular range of 2-3 nm^{-1}, reminiscent of conventional ionomers. Figure 2 shows a representative variable-temperature scattering data for PEG600 -100% Na. For the fully sulfonated ionomers neutralized by cesium cations, the broad peak at 7 nm^{-1} gradually diminishes as the temperature increases, and a new peak also appears at q ~ 2-3 nm^{-1}. The intensity of the new peak decreases as the sulfonation level decreases and the peak appears broader and asymmetric due to the overlap with the upturn.

There is no new peak appears at high temperature for materials with 0% sulfonation, which is expected. As the temperature increases, the amorphous halo of PEG-based ionomers shifts to the lower-angular position in all ionomers, which is caused by the thermal expansion of the polymer. The morphology of ionomers is reversible when the system is cooled down, and the scattering profile at room temperature after cooling is identical to that of room temperature before heating (Figure 2). The appearance of "ionomer peak" at high temperature is attributed to the formation of new ionic aggregates. A mechanism is proposed to explain the ionic association behavior as a function of temperature. These results will provide new insights into the development of advanced single-ion conductors for lithium-ion batteries.

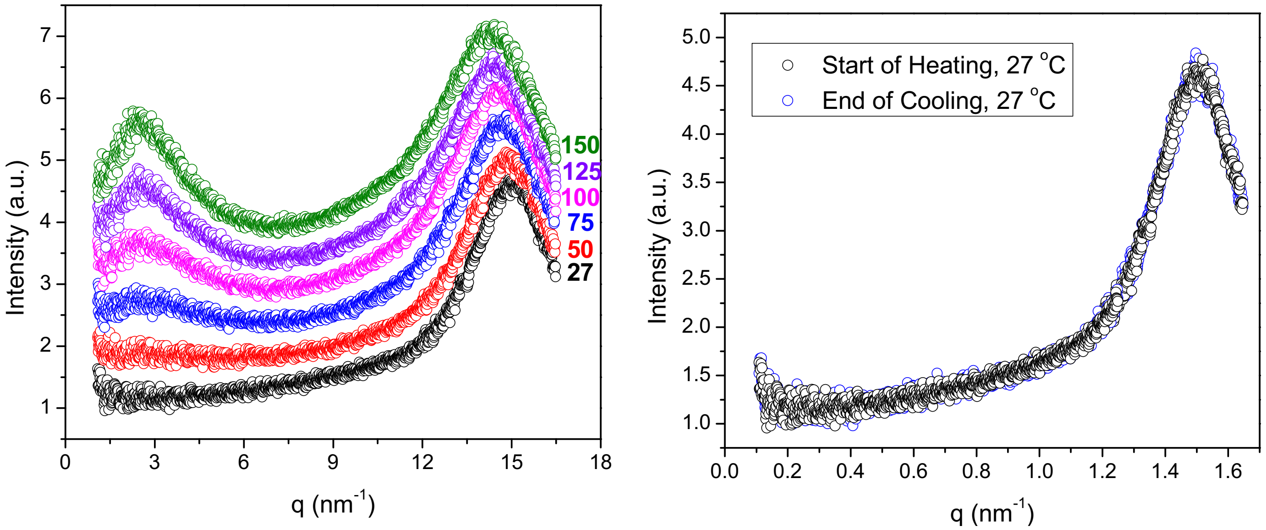

Figure 2. X-ray scattering data for PEG600 – 100% Na as a function of temperature: 27, 50, 75, 100, 125, 150 °C (left). Room temperature X-ray scattering data for PEG600 -100% Na before and after heating (right).

References

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