

Hierarchical Ion-Conducting Materials Based on Polymer-Aligned Nanoparticles within Poly(vinyl benzyl methoxy poly(ethylene oxide) ether)-*block*-polystyrene Diblock Copolymer

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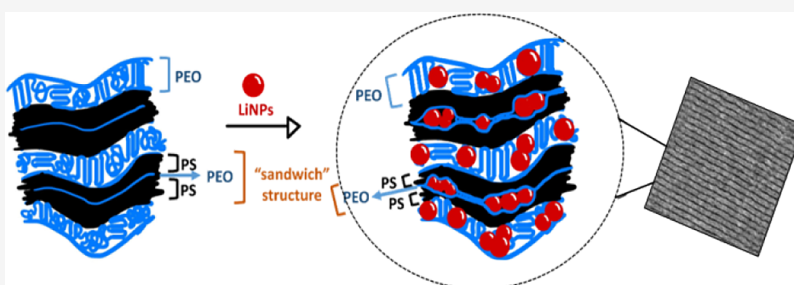
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ABSTRACT: Solid polymer electrolytes based on poly(ethylene oxide) (PEO) are promising alternatives to liquid electrolytes for safer lithium-ion batteries. Here, we report hierarchical solid polymer electrolytes obtained by selectively incorporating lithium sulfonamide-functionalized polymer nanoparticles (LiNPs) into a microphase-separated poly(vinyl benzyl methoxy poly(ethylene oxide) ether)-*block*-polystyrene block copolymer. Transmission electron microscopy (TEM), atomic force microscopy (AFM), and small-angle X-ray scattering (SAXS) demonstrate that the phase-segregated lamellar morphology of the block copolymer is preserved upon nanoparticle incorporation. Notably, the LiNPs preferentially localize within the poly(ethylene glycol)-rich lamellae, generating hierarchical structures with ordering across multiple length scales arising from block copolymer self-assembly, selective nanoparticle organization, and poly(ethylene glycol) crystallization. Differential scanning calorimetry (DSC) reveals that the crystallinity of the poly(ethylene glycol) phase depends strongly on nanoparticle loading and plasticizer content. These hierarchical electrolytes exhibit high ionic conductivity, which is further enhanced by the addition of sulfolane as a plasticizer. These results elucidate the interplay between hierarchical morphology, phase crystallinity, and ion transport in block copolymer-based solid electrolytes, providing design guidelines for mechanically robust solid electrolytes with enhanced transport performance.

1. INTRODUCTION

Solid polymer electrolytes (SPEs) have attracted significant attention as a viable solution to address safety concerns arising from the use of liquid electrolytes in lithium-ion batteries (LIBs).^{1–6} In particular, poly(ethylene oxide) (PEO) is among the most studied polymer matrices in the field.^{1,2,6,7} However, the low ionic conductivity at room temperature (10^{-8} – 10^{-6} S/cm) and the low lithium transference number (ca. 0.2–0.3) of the resulting SPEs obtained by mixing PEO with lithium salts remain an obstacle.^{5,8,9} The main reason for this limitation in PEO-based SPEs is the crystallinity of the polymer at room temperature,^{8,9} which generally decreases with increasing lithium salt concentration, along with an increase in ionic conductivity. However, this decrease is inevitably accompanied by a drop in mechanical properties.⁵ Among the different strategies to solve the issue,^{10–14} the use of microphase-separated block copolymers has gathered significant

attention because of the possibility to achieve robust SPEs wherein mechanical integrity is imparted by a rigid block and ionic conduction occurs within a softer, transport-active block.^{15–19}

Thus, the combination of polystyrene (PS) and poly(ethylene oxide) or poly(ethylene glycol) in block copolymers is currently among the most popular strategies in the field, in which PEO domains are responsible for ion conduction and styrene domains provide mechanical rigidity.^{20–26} Butzelaar et al.¹⁸ established a

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straightforward synthesis of a block copolymer based on PEO and PS, named poly(vinyl benzyl methoxy poly(ethylene oxide) ether)-*block*-polystyrene (PVBmPEO2000-*b*-PS). This diblock copolymer was combined with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) to form self-standing films that exhibited ionic conductivity of ca. 1.6×10^{-5} S/cm at room temperature. Later, the block copolymer and LiTFSI system were used in combination with two different ionic liquids, only compatible with the PEO, to improve the ionic conductivity by two orders of magnitude (1.0×10^{-3} S/cm at 40 °C).¹⁹

Another limitation of PEO polymer electrolytes is their low lithium transference number due to the high mobility of the anions. Here, the so-called single-ion-conducting polymers are becoming a very popular strategy. In single-ion-conducting polymers, the anion is covalently bonded to a cross-linked network and, thus, is constrained, allowing only the mobility of the lithium ions.^{27–30} Furthermore, restricting anion mobility effectively mitigates battery polarization and suppresses lithium dendrite growth.^{17,27,31} In this context, Porcarelli et al. reported the preparation of polymeric lithium-functionalized nanoparticles (LiNPs) via emulsion polymerization, in which lithium ions are the only freely mobile species.³² These LiNPs were used as a brick to construct single-ion-conducting all-polymer nanocomposites by blending with PEO.³³ The favorable interfacial interactions between the ethylene oxide groups and the LiNP surface ensured their dispersion within the polymer network.

In fact, the inclusion of nanoparticles into polymeric matrices is an increasingly popular strategy, often pursued to obtain mechanically improved systems.^{32–35} In a pioneering work, Balsara et al. added nanoparticles to a PS-*b*-PEO and lithium salt system to improve ionic conductivity, resulting from a morphological change driven by the nanoparticles.²⁵ Thus, the introduction of nanoparticles can affect mechanical properties, crystallinity, morphology, and electrochemical properties.³⁶ More recently, the use of polymeric LiNPs in combination with different plasticizers has been exploited to prepare quasi-solid-state single-ion polymer electrolytes (SIPEs). Gallastegui et al. used carbonates and sulfolane as plasticizers, and the resulting electrolytes showed ionic conductivity values of 2.9×10^{-4} and 2.3×10^{-5} S/cm at 85 °C.¹³ Meanwhile, Berzosa et al. investigated LiNPs with different compositions to improve the ionic conductivity and the resistance toward lithium dendrite

growth, achieving stable plating and stripping in lithium symmetrical cells up to 0.2 mA/cm² and cycling with an NMC cathode at 45 °C.¹⁴ Indeed, nanoparticles were used to obtain an all-polymer nanocomposite solid electrolyte by mixing PEO and LiNPs, targeting an improvement of the SPE mechanical properties.³³ Finally, Olmedo-Martínez et al.³⁷ investigated the distribution of the LiNPs in the PEO matrix, revealing that the ordering of LiNPs within interlamellar regions of PEO, by controlling the crystallization rate, allows us to achieve superior ionic conductivity compared to the nonordered system.

In this work, self-assembled poly(vinyl benzyl methoxy poly(ethylene oxide) ether)-*block*-polystyrene block copolymer was used as a matrix for the selective dispersion of LiNPs in one of the phase-separated blocks. More specifically, the selective positioning of LiNPs within one of the phase-separated blocks was studied using different techniques. The LiNPs ordering within the nanocomposite were confirmed by transmission electron microscopy (TEM), atomic force microscopy (AFM), and small-angle X-ray scattering (SAXS), and crystallinity was studied by differential scanning calorimetry (DSC). Finally, the effect of morphology on the ionic conductivity of the hierarchical materials was analyzed in the presence of a plasticizer.

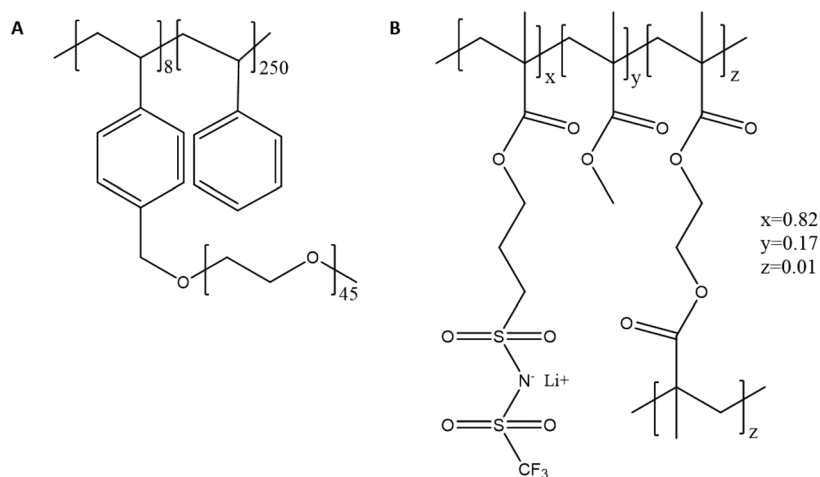
2. EXPERIMENTAL SECTION

2.1. Materials

Poly(vinyl benzyl methoxy poly(ethylene oxide) ether)-*block*-polystyrene (PVBmPEO2000-*b*-PS) was obtained by sequential RAFT polymerization as described in the literature.^{18,19} Regarding its molecular weight, we calculated the theoretical molecular weight based on the polymerization degree of each block and the EO units of the starting monomer. The total molecular weight was 43,079 g/mol. The fraction of the PEO (*f*) in the diblock copolymer is 37% by weight, considering its molecular weight to be 1,980 g/mol in each of the 8 PEO-PS blocks. Its chemical structure is depicted in Results and Discussion Section Scheme 1A.

The lithium sulfonamide-functionalized polymeric nanoparticles (LiNPs) were obtained by drying a polymer nanolatex produced by emulsion polymerization, as reported in our previous work.¹⁴ In that study, the lithium content was determined by inductively coupled plasma mass spectrometry (ICP-MS) to be 8.7 mg/g of nanoparticles. At the same time, DLS measured an average hydrodynamic diameter of 24 nm. Later, in the Results and Discussion Section, we present the

Scheme 1. Chemical Structures of (A) Block Copolymer and (B) Lithium-Functionalized Polymeric Nanoparticles



LiNP diameter measurements by TEM and AFM. The chemical structure of LiNPs is depicted in Scheme 1B.

For the preparation of the films, acetonitrile (ACN), tetrahydrofuran (THF), sulfolane (99%), propylene carbonate (PC) (99%), and tetraethylene glycol (G4) (99%) were purchased from Sigma-Aldrich.

2.1.1. Preparation of the Films for the Ordering of the LiNPs into the PEO within the Block Copolymer. The neat PVBmPEO2000-*b*-PS (or BCP, as we will refer to it later) and the composite films with LiNPs were obtained by solvent casting (from both ACN and THF in the case of the neat BCP) first at room temperature for ca. 24 h and then under vacuum at 35 °C for 3 days to remove any remaining solvent. Subsequently, a thermal protocol was applied to ensure the erasure of thermal history. First, samples were heated to 160 °C, a temperature that is higher than $T_m + 30$ °C (above the T_m of the PEO and the T_g of the PS) at 20 °C/min. Then, using the same rate, they were cooled to a low temperature (−40 °C) and heated up to room temperature (RT). The samples used for TEM, AFM, and SAXS were prepared in DSC aluminum pans. The samples used for EIS were thermally treated in a Memmert UF30plus oven.

To prepare the nanocomposites, the BCP was dissolved in ACN and LiNPs were added in different concentrations, i.e., 10%, 20%, and 35% by weight relative to PEO. The highest concentration at which the nanoparticles dissolved was 35 wt %; higher concentrations led to visible agglomeration. For the PVBmPEO2000-*b*-PS with 35 wt % LiNPs, the sulfolane plasticizer was added in concentrations of 30, 40, and 60% by weight with respect to the LiNPs and the PEO. Sulfolane was added together with LiNPs. Solutions containing LiNPs alone and with sulfolane underwent ultrasonication for 30 min and magnetic stirring overnight before solvent casting.

2.2. Transmission Electron Microscopy (TEM)

A Leica EM UC7 cryo-ultramicrotome was used to obtain approximately 70 nm thick polymer sections from the thermally treated samples. The samples were microtomed at −80 °C via a 35 °C Diatome diamond knife. The sections were then deposited on 300-mesh copper grids coated with lacey carbon. Later, the grids were brought up to room temperature under vacuum. Next, sections were stained with RuO₄ for 10 min in the case of the neat block copolymer and 30–180 s for samples doped with LiNPs. Microscopic characterization was conducted using either JEOL JEM-3200FSC (300 kV) or Tecnai 12 (120 kV). In the case of acquisitions taken via JEOL JEM-3200FSC, the specimen was kept at −174 °C during the imaging process. Additionally, micrographs were acquired using an omega-type zero-loss energy filter (a slit width of 30 keV). Pictures were recorded via a Gatan Ultrascan 4000 CCD (JEOL JEM-3200FSC) or Gatan Ultrascan 1000 CCD (Tecnai 12).

2.3. Atomic Force Microscopy (AFM)

The morphology of the PVBmPEO2000-*b*-PS block copolymer and its nanocomposites with LiNPs was also studied by AFM using a Dimension Icon with a Nanoscope VI controller (Bruker). The AFM measurement was performed in tapping mode using an integrated silicon TESP-V2 tip/cantilever with a resonance frequency of ~320 kHz. Scan rates ranged from 0.8 to 1 Hz/s. Different areas of each sample were scanned to choose representative AFM images. Cross-sections of each sample after DSC thermal treatment, as addressed in Section 2.5, were obtained by cutting with a diamond knife using a Leica Ultracut R ultramicrotome at room temperature.

2.4. Small-Angle X-ray Scattering (SAXS)

SAXS experiments were carried out at room temperature after a thermal treatment, which consisted of heating the samples to 160 °C to erase the thermal history, cooling to −40 °C, and heating back to RT. These were performed at 20 °C/min, and DSC was used on samples encapsulated in aluminum pans. The experiments were performed at the BL11-NCD beamline in the ALBA synchrotron (Cerdanyola del Vallés, Spain).

2.5. Differential Scanning Calorimetry (DSC)

The crystallization of the neat PVBmPEO2000-*b*-PS and of membranes containing different concentrations of LiNPs was studied using a Perkin-Elmer 8000 calorimeter. The DSC is equipped with an Intracooler 2 cooling system that operates under a nitrogen atmosphere at a gas flow rate of 20 mL/min. The calibration was performed with indium and tin standards. Samples were weighed and sealed in aluminum standard pans (ca. 5 mg).

The protocol consisted of heating the material up to a sufficiently high temperature, i.e., 160 °C (over $T_m + 30$ °C, above the T_g of the PS), to erase the thermal history for 3 min. Then, the samples were cooled to a low temperature (−50 °C for 1 min) and heated again to over $T_m + 30$ °C.

2.6. Electrochemical Characterization

For ionic conductivity measurements, an Autolab 302N potentiostat/galvanostat (Metrohm AG) equipped with a temperature controller (Microcell HC station) was used. The solvent-cast and thermally treated films were placed between two stainless steel electrodes (surface area of 0.5 cm²) and measured over a range of temperatures (25–100 °C). The Nyquist plots were obtained by electrochemical impedance spectroscopy (EIS) using a 10 mV perturbation voltage in a frequency range of 100 kHz to 1 Hz.

The electrochemical stability window (ESW) was investigated by linear sweep voltammetry (LSV), performing separate anodic (Li vs Stainless steel, SS) and cathodic (Li vs Copper, Cu) scans at 1 mV/s^{−1} scan velocity at 80 °C. The investigated potential range was between −0.5 and 5 V vs Li⁺/Li.

Li⁺ transference number (t_{Li^+}) was determined at 80 °C with a Li metal symmetrical cell subjected to a 0.20 mV polarization bias after an equilibration time. EIS was performed before and after the application of the external potential, and the Bruce–Vincent method was used to calculate the t_{Li^+} , following the equation:³⁸

$$t_+ = \frac{I_{ss}(\Delta V - (R_{b0} \times I_0))}{I_0(\Delta V - (R_{bss} \times I_{ss}))}$$

Lithium plating and stripping measurement was conducted with a Li metal symmetrical cell at 80 °C at 0.1 mA/cm² (1 h of plating and 1 h of stripping per cycle).

ESW, t_{Li^+} , and galvanostatic cycling measurements were conducted using coin cells CR2032 assembled in an argon-filled glovebox (H₂O and O₂ content ≤ 0.1 ppm) to avoid oxygen and moisture contamination.

3. RESULTS AND DISCUSSION

The hierarchical ion-conducting materials investigated here were based on a PVBmPEO2000-*b*-PS block copolymer and lithium sulfonamide-functionalized cross-linked poly(methyl methacrylate) nanoparticles (LiNPs). The structure of the BCP obtained by sequential RAFT polymerization is characterized by a PEO-type block for ionic conductivity and a PS block for the mechanical properties as illustrated in Scheme 1A.^{18,19} The LiNPs (Scheme 1B) were obtained by emulsion polymerization as reported in our previous work.¹⁴ The hierarchical materials were prepared by simple solvent casting a blend of both components (block copolymer and LiNPs) following the procedure described in the Experimental Section.

However, before investigating the effect of the LiNP addition, we studied the bulk morphology of the neat BCP and the role of the solvent on the orientation upon thermally treating the samples. Since all films were thermally treated after solvent casting, the direct influence of solvent-induced ordering

near the substrate cannot be unambiguously inferred from the TEM micrographs. Moreover, the thermal treatment is essential for a highly ordered, lamellar nanostructure. The bulk morphology captured via TEM prior to thermal annealing can be found in the Supporting Information, Figure S1. Nevertheless, distinct changes in alignment were observed in the samples prepared using different solvents. Controlling orientation is critical, as unfavorable alignments can disrupt continuous ion-conducting pathways and reduce the fraction of material contributing to ion conduction.^{39–44} In neat BCP films cast from ACN (Figure 1A), which is a selective solvent for the PEO,⁴⁵ TEM revealed a highly favorable, long-range ordering of lamellae oriented predominantly perpendicular to the substrate throughout the entire bulk. Conversely, films cast from THF (Figure 1B), which is a rather good solvent for both PEO and PS,⁴⁶ exhibited a fundamentally different alignment. While parallel stacking was observed near the interface, the bulk of the material displayed a randomized orientation distribution.

These distinct, solvent-driven morphological alignments observed via TEM are further corroborated by 2D SAXS patterns, with pronounced intensity maxima consistent with the perpendicular lamellar ordering for the case of ACN (Figure 1, insets). We hypothesize that, in the case of the ACN solvent-cast sample, the self-assembly process may be initiated from the formation of micellar-like structures with a PS-rich core and a PEO-rich corona. These preformed anisotropic structures, along with the interfacial constraints and gradual solvent evaporation, likely govern the final alignment, which is triggered by the thermal treatment. The lower selectivity of THF toward the PEO may lead to differences in the self-assembly pathway that ultimately lead to the randomized lamellar morphology. Consequently, ACN was selected for the preparation of the hierarchical ion-conducting materials, including LiNPs.

It is well known that due to the immiscibility of the PS and PEO blocks, they tend to segregate into microdomains.^{20,21,25,26} In our case, we have chosen a block copolymer with a segregation strength high enough to separate into microphases.^{18,19} On the other hand, the polar sulfonamide-functional LiNPs are highly compatible with the poly(ethylene glycol)^{33,37} domain

but not with the apolar polystyrene domain. Hence, the polymer nanoparticles are expected to assemble within the PEG/PEO microdomains.

To corroborate this hypothesis, we performed TEM of our nanoparticle-block copolymer hierarchical nanocomposites (Figure 2). It is clear from Figure 2A (as well as Figure 1) that the neat block copolymer exhibits a well-defined lamellar morphology, characterized by the alternation of light and dark domains. The RuO₄ preferentially stains the PEO block; hence, the lighter regions correspond to the PS block microdomains, while the darker regions correspond to the PEO block microdomains. The presence of a highly ordered lamellar arrangement indicates strong microphase separation between the PS- and PEO-type blocks, driven by the thermodynamic incompatibility of the two polymers and constrained by the covalent linkage between them. Theoretically, the segregation of the system depends on the volume fraction (f_v) of the monomers and the product χN , where χ is the Flory–Huggins interaction parameter (dependent on temperature) and N corresponds to the polymerization degree.^{47–49} According to Leibler, in the case of symmetric and close-to-symmetric diblock copolymers ($f_v \approx 0.5$), a χN product higher than 10.5 leads to the formation of a lamellar morphology, while a lower value leads to a disordered state.⁴⁷ However, with asymmetric diblock copolymers, depending on the volume fraction f_v , a higher χN product may be required to reach the lamellar morphology, and other morphologies such as hexagonal or body-centered-cubic are possible at lower χN products. In our case, the theoretical estimation of the χN product was not possible; nevertheless, the difference in the solubility parameter, δ , of PEO and PS⁵⁰ and the high molecular weight of the employed copolymer suggest a high χN product, evidenced by the lamellar morphology observed through TEM (Figures 1 and 2A).

Moreover, the PS block microdomains contain a thin, difficult-to-spot dark line, which we believe corresponds to PEO (see Figure 2A). ImageJ was used to measure both the PEO and PS block microdomains, obtaining values of 6 ± 1 and 16 ± 2 nm, respectively. It is important to note that the thin PEO microdomain within the PS domain was too thin to

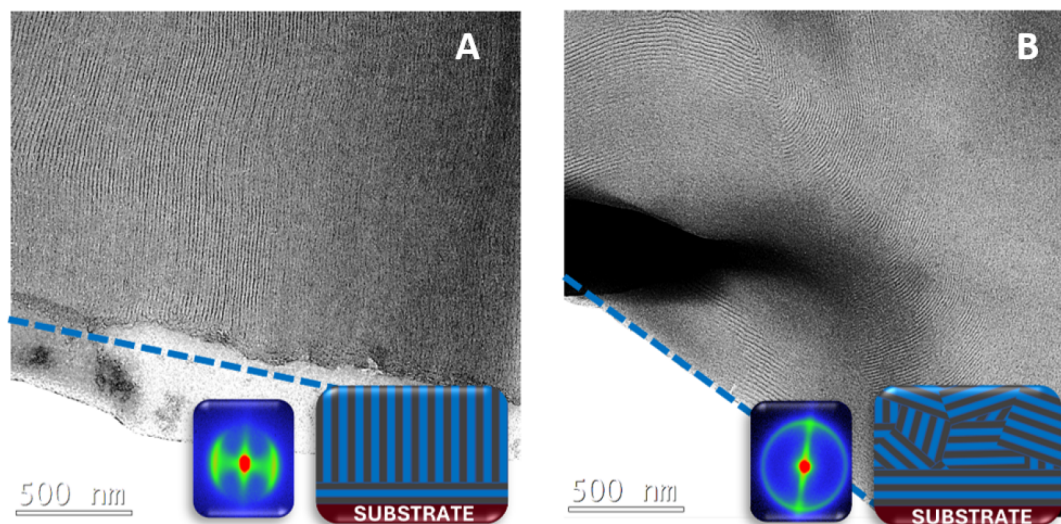


Figure 1. Morphology of BCP cast from (A) ACN and (B) THF near the substrate/BCP interface (marked by the blue line). Insets show 2D SAXS patterns of the samples in the cross-sectional plane. Schemes illustrate macroscopic ordering of the films.

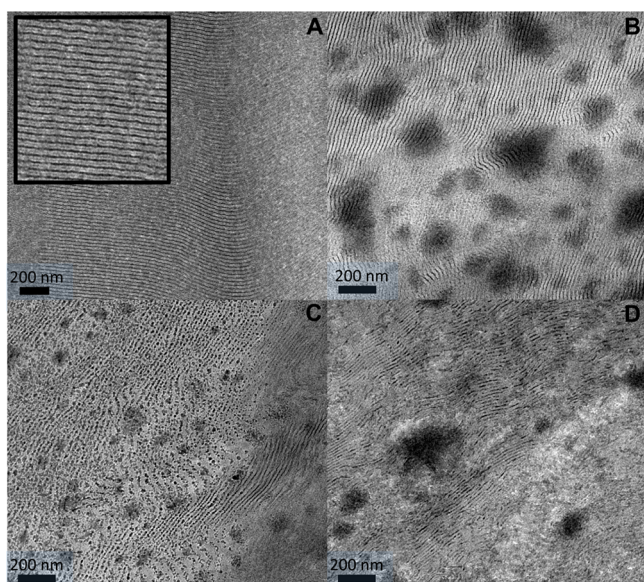


Figure 2. TEM micrographs of (A) neat PVBmPEO2000-*b*-PS (or BCP), (B) BCP with 10 wt % LiNPs, (C) BCP with 20 wt % LiNPs, and (D) BCP with 35 wt % LiNPs.

measure; hence, the 16 nm value corresponds to the whole “sandwich” structure (see Scheme 2A below).

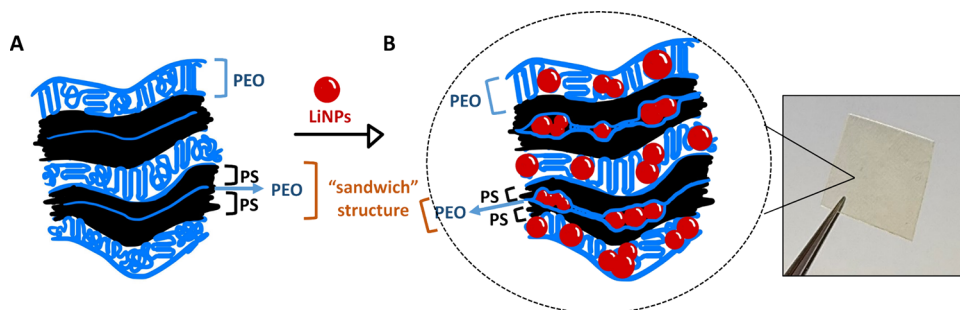
Upon incorporation of LiNPs, we assume the χN product varies, as it would if a lithium salt was added.⁵¹ However, the system remains strongly segregated into the characteristic lamellar morphology (see Figure 2B–D) wherein the thickness of the PEO microdomains has apparently increased for most samples in comparison to the PEO microdomains of the neat BCP (Figure 2A). This observation is consistent with the preferential localization of LiNPs within the PEO phase likely due to favorable interactions between the lithium-containing nanoparticles and the polar ether groups. As nanoparticles enter the PEO domains, they effectively swell this lamellar phase, increasing its thickness. Importantly, despite the incorporation of LiNPs and the associated swelling of the PEO layers, the overall lamellar morphology remains preserved. The measurements of each microdomain through ImageJ are as follows: the BCP with 10 wt % LiNPs has a PS domain of 12 ± 2 nm, and the PEO domain is 5 ± 2 nm; the BCP with 20 wt % LiNPs has a PS domain of 13 ± 5 nm and a PEO domain of 8 ± 3 nm. Lastly, the PS domain of the BCP containing 35 wt % LiNPs is 11 ± 3 nm and the PEO domain is 8 ± 2 nm. With increasing concentration of LiNPs, these are incorporated not only

into the easily observable PEO microdomain but also into the thin microdomain that remains “inside” the PS block domain (see Scheme 2B). Hence, when nanoparticles are located there, these PEO microdomains within the PS thicken, slightly shrink the PS domain, and make it easier to measure. In other words, in the neat BCP, the PS domain was measured as a “sandwich” containing PS, the thin PEO microdomain, and PS. As the nanoparticle concentration increases, measuring only the PS microdomain becomes easier. Thus, with the highest concentration of LiNPs, the measured distance of the PS domains is smallest (ca. 11 nm), while the system containing the smallest concentration of LiNPs (i.e., 10 wt %) still shows many areas where the “sandwich” cannot be measured separately, consequently obtaining a distance of ca. 12 nm. As for the PEO microdomain, it increases overall with the addition of the nanoparticles. An important observation is that although the LiNPs are only compatible with PEO, they do not integrate homogeneously into the system; they form aggregates, which explains the many “empty” PEO areas, most notable at 10 wt % LiNPs but present at all concentrations. For this very reason, the error in the thickness measurements on the TEM micrographs in the samples containing LiNPs is considerably higher than that measured for the neat BCP.

Moreover, it should be noted that the perpendicular lamellar alignment obtained using ACN as a solvent is retained despite the addition of nanoparticles. Indeed, TEM analysis on samples doped with 30 wt % LiNPs was performed and is available in the Supporting Information. For comparison purposes, such samples were again prepared using both ACN and THF (see Figure S2).

The alignment of the LiNPs was clear from the TEM images. Next, SAXS was used to further quantify the interlamellar distances of our materials. These SAXS results are shown in Figure 3, using the Lorentz-corrected intensity as a function of the scattering vector (q). The neat block copolymer yields two signals at $1q$ and $2q$. This indicates that the morphology is lamellar,⁵² as seen previously in the TEM micrographs (Figures 1 and 2). In Figure 3, a scheme of this morphology is depicted, with black corresponding to the PS domains and blue corresponding to the PEO domains. Then, we can observe the interlamellar distance increasing with the addition of LiNPs. The distance increases from 22 nm (neat BCP) to 24–26 nm depending on the concentration of LiNPs (calculated $d = (2\pi n)/q^*$ as reported in the literature⁵³). These findings show slight variations relative to the TEM measurements obtained with ImageJ. While the long period in the neat BCP is comparable (22 nm in SAXS and TEM), the systems containing LiNPs show larger differences. The long period of the BCP with 10 wt % LiNPs is 24 nm according to SAXS, while TEM

Scheme 2. Schematic Illustration of the “Sandwich” Structure Containing PS, the Thin PEO Microdomain, and PS in (A) Neat BCP and (B) BCP Containing LiNPs



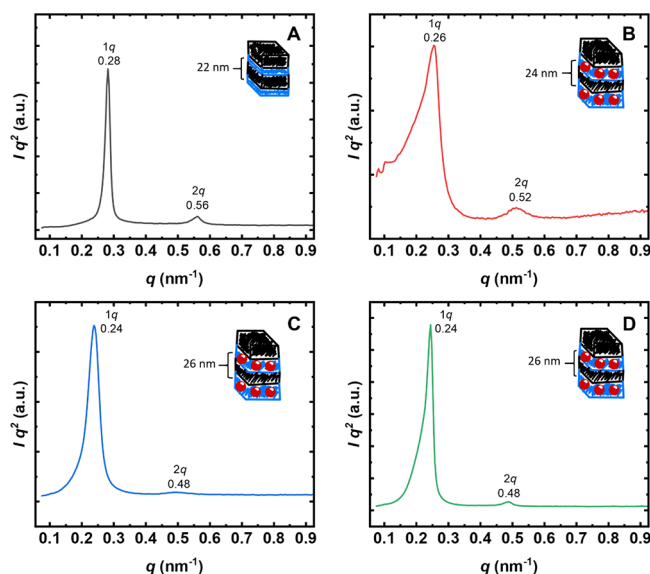


Figure 3. Lorentz-corrected SAXS of the PVBmPEO2000-*b*-PS with different concentrations of LiNPs: (A) neat BCP, (B) BCP with 10 wt % LiNPs, (C) BCP with 20 wt % LiNPs, and (D) BCP with 35 wt % LiNPs.

showed ca. 18 nm; 20 wt % LiNPs exhibits an interlamellar distance of 26 nm according to SAXS and ca. 24 nm according to TEM. Lastly, SAXS shows a distance of 26 nm, and TEM shows 19 nm for the BCP with 35 wt % LiNPs. As previously stated, the LiNPs do not locate homogeneously in the PEO microdomains, leading to considerable differences, most notably using TEM and depending on the measured area. Overall, SAXS yields more representative results for the bulk. Similarly, the SAXS distribution is broader for samples containing LiNPs due to the inhomogeneous placement of LiNPs within the PEO block microdomains.

The influence of LiNPs on the self-assembly of the BCP was further investigated using AFM (Figure 4). Diamond-knife-cut transverse cross-sections of each sample were analyzed. As in the case of TEM, the well-defined lamellar structure of the self-assembled PVBmPEO2000-*b*-PS block copolymer is shown in Figure 4A, where lighter lamellae correspond to the PS block microdomains and darker lamellae to the PEO block microdomains. Upon addition of the LiNPs, the AFM phase images (Figure 4B–D) show small, spherical nanoparticles within the dark PEO microphase located near the interface between self-assembled blocks of BCP.⁵⁴ The average size of the LiNPs is 6 ± 1 nm according to AFM. As the nanoparticle concentration increases, the dark PEO microdomains appear thicker due to aggregation, particularly at 35 wt % LiNPs, where individual nanoparticles cannot be resolved (see Figure 4D). Despite the thickening of some of the PEO block microdomains, the morphology remains lamellar. Hence, these images confirm the findings above (Figures 1–3).

Next, the crystallinity of the neat copolymer as well as the films containing 10, 20, and 35 wt % LiNPs was studied by DSC. The crystallization temperature for the PEO within the BCP is ca. 13 °C, while the melting occurs at 52 °C, at the studied cooling rate of 20 °C/min (Figure 5). In a PEO homopolymer of similar molecular weight to the PEO side chain of the BCP (2 kg/mol), these values are $T_c \approx 29$ °C and $T_m \approx 60$ °C, using the same rate (see Figure S3). Due to the strong segregation and the PS block microdomains being vitrified over

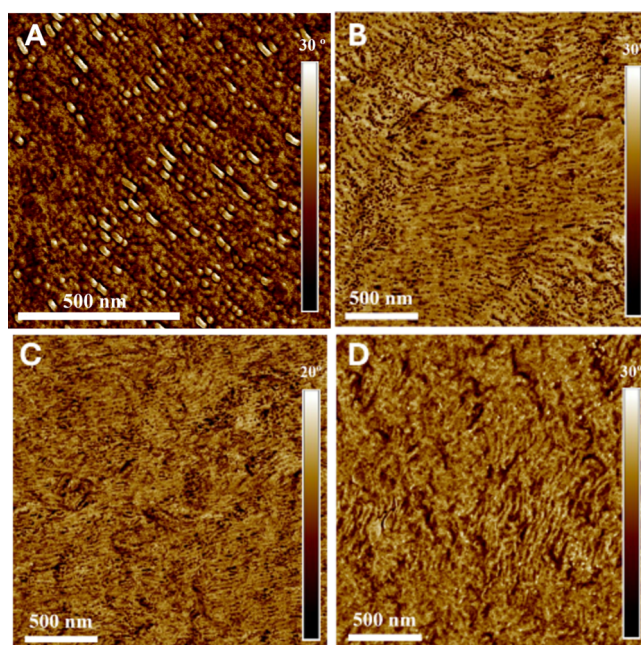


Figure 4. AFM phase images of (A) neat BCP, (B) BCP + 10 wt % LiNPs, (C) BCP + 20 wt % LiNPs, and (D) BCP with 35 wt % LiNPs.

the temperature range in which the PEO crystallizes (the T_g of the PS is ca. 100 °C),^{18,19} the PEO should be confined within its microdomains. Such confinement appears to decrease the PEO crystallization ability, thus yielding a lower T_c , lower T_m , and crystallinity degree.

As seen in Figure 5, the neat PVBmPEO2000-*b*-PS has a relatively high crystallinity of 65% due to crystallization of the PEO side chains, although lower than its homopolymer version (78%). The degree of crystallinity was calculated by measuring the melting enthalpy ΔH_m , which is the integration of the heat flow under the melting endotherm, and applying it to the equation $X_c = \frac{\Delta H_m}{f \Delta H_m^0} \times 100$, where f is the weight fraction of the PEO in the sample and ΔH_m^0 is the PEO equilibrium melting enthalpy, which is a theoretical value that corresponds to the melting enthalpy of a perfect crystal; the value for ΔH_m^0 of PEO is 214 J/g.¹⁷ With increasing concentration of LiNPs, the crystallinity decreases to 59%, 46%, and 16% (with 10, 20, 35 wt % LiNPs). This decrease was expected since the LiNPs strongly interact with the PEO and hinder the packing of the chains and their ability to crystallize into an ordered state.³³

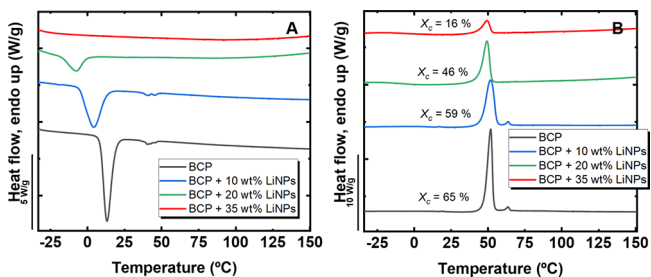


Figure 5. (A) DSC cooling scans from the melt and (B) subsequent heating scans of PVBmPEO2000-*b*-PS as well as the BCP with 10, 20, and 35 wt % LiNPs.

Ionic conductivity measurements were attempted from 25 up to 100 °C. However, as shown in Figure 6, measurements were possible only from 60 °C upward. Below the melting point of PEO, i.e., below ca. 50 °C, the crystallinity within the PEO phase hinders ion conduction and makes the sample too rigid to be properly measured. Samples must have good contact with the electrodes, which is difficult when films are very rigid. The melting transition marks the threshold at which measurements can be taken. However, at the melting point (50 °C), contact between the sample and electrodes is still inadequate for accurate results. Therefore, only measurements obtained at temperatures above the melting transition of the PEO (from 60 to 100 °C) are depicted in Figure 6.

Overall, increasing the nanoparticle load increases ionic conductivity (see Figure 6). For instance, the film containing 10 wt % LiNPs has the lowest ionic conductivity, i.e., 7.4×10^{-8} S/cm at 80 °C. As depicted in Figure 6, the ionic conductivity increases following the increment of LiNPs, achieving values of 5.0×10^{-7} and 2.8×10^{-6} S/cm at 80 °C for the samples containing 20 and 35 wt % LiNPs, respectively. In addition, over the measured temperature range (from 60 °C upward), sample crystallinity does not restrict ion movement, and conductivity increases with temperature. It is worth noting that, across all investigated polymer electrolytes, ionic conductivity is determined solely by the lithium cation mobility, while the anions are immobilized in the LiNPs, thereby ensuring single-ion conduction in the SPEs.

Despite the focus of the work being the study of the structure–property relationship of an ion-conducting material, further electrochemical characterization has been carried out on sample PVBmPEO2000-*b*-PS with 35% of LiNPs to provide a comprehensive overview of the material for energy storage applications. Linear sweep voltammetry (LSV) performed at 80 °C revealed that the polymer electrolyte is stable against oxidation up to ≈ 4.5 V vs Li^+/Li . Furthermore, no visible reduction peaks were observed during the cathodic scan prior to the onset of lithium plating on copper at ≈ 0 V vs Li^+/Li , as shown in Figure S4A. The Lithium transference number t_{Li^+} was measured at 80 °C following the Bruce–Vincent method.³⁸ The polymer electrolyte showed a t_{Li^+} of 0.93, in line with the single-ion-conducting nature of the conducting material (see Figure S4B). Additionally, galvanostatic lithium plating/stripping at 0.1 mA/cm² and 80 °C revealed stable cycling over time with a limited increase of overpotential of 0.024 V after 100 cycles, highlighting the robust electrochemical compatibility of the polymer electrolyte toward the lithium metal anode (see Figure S4C).

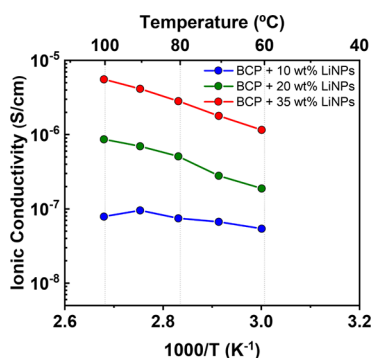


Figure 6. Ionic conductivity results for PVBmPEO2000-*b*-PS with different concentrations of LiNPs.

To improve the temperature range of application of the obtained hierarchical materials as solid electrolytes and to increase ionic conductivity while maintaining single-ion character, sulfolane was added at different concentrations (weight % relative to PEO and LiNPs) as a plasticizer. The best sample, PVBmPEO2000-*b*-PS containing 35 wt % LiNPs, was selected to investigate the effect of the plasticizer on the ionic conductivity and crystallinity. The sulfolane was added in concentrations of 30%, 40%, and 60% in weight. The TEM, AFM, and SAXS results are provided in the Supporting Information, Figures S5–S7. The DSC and ionic conductivity results are shown below (Figure 7).

Sulfolane is a widely used small-molecule plasticizer in lithium batteries due to its thermal stability, high dielectric constant, and oxidation potential.^{55–57} For these reasons, it was combined with the BCP. The addition of sulfolane to the system is expected to promote amorphization of the PEO phase, with a consequent decrease in crystallinity and an increase in lithium-ion mobility at temperatures below the melting transition. As shown in Figure 7C, adding sulfolane allowed the polymer electrolyte to be used over a wider temperature range due to films becoming less rigid and improving sample-electrode contact. Specifically, across all compositions, the ionic conductivity at 25 °C ranged from 1×10^{-7} to $\sim 7 \times 10^{-7}$ S/cm. However, we observed an increased crystallinity (Figure 7A,B). Namely, as reported in Figure 7B, the degree of crystallinity of the sample containing 35 wt % LiNPs increases from 16% to 33% after the addition of 30 wt % sulfolane and to 30% after the addition of 40 and 60 wt % plasticizers. When the plasticizer is added, it probably swells the PEO domains, as seen in SAXS experiments (see Figure S7), and most likely promotes segmental chain motion, acting like a plasticizer for PEO. The increased chain mobility enhances the crystallization rate below the melting point. At temperatures above T_m of PEO (i.e., from 50 °C upward), PEO should contribute to the conductivity more, and we would expect to see a slope change in the ionic conductivity vs temperature plots (Figure 7C). However, despite the thickening of the PEO block microdomains (Figure S7), we believe that due to the overall restricted PEO microdomain area and relatively low crystallinity, its melting does not allow the LiNPs to move/realign and, thus, the trend does not dramatically change. Notably, this strategy enabled us to achieve satisfactory ionic conductivity in a wide range of temperatures (10^{-7} S/cm at 30 °C and 10^{-6} S/cm at 80 °C) while maintaining the polymer electrolyte's film-forming ability.

Considering these interesting results, we decided to extend our investigation to several well-known plasticizers used in polymer electrolytes, such as tetraethylene glycol dimethyl ether (tetraglyme, TEGDME) and propylene carbonate (PC). DSC and conductivity results proved that both additives have similar effects on crystallinity, which increases upon the addition of the plasticizer (see Figure S8). This phenomenon is typical in other polymers, such as poly(lactic acid) (PLA).^{58,59} However, in the case of PEO, these types of plasticizers tend to decrease its crystallinity.^{60–63} Our results show the opposite trend: the crystallization of PEO increases when plasticized, likely because it releases the PEO from confinement to its microphase within the BCP. This confinement probably slows the crystallization kinetics of unplasticized PEO and reduces its crystallinity. As we previously mentioned, the degree of crystallinity of a PEO homopolymer of similar molecular weight is higher than in the case of the PEO within our block copolymer (78% vs 65%, in Figure S3). The addition of a small-molecule plasticizer (either sulfolane,

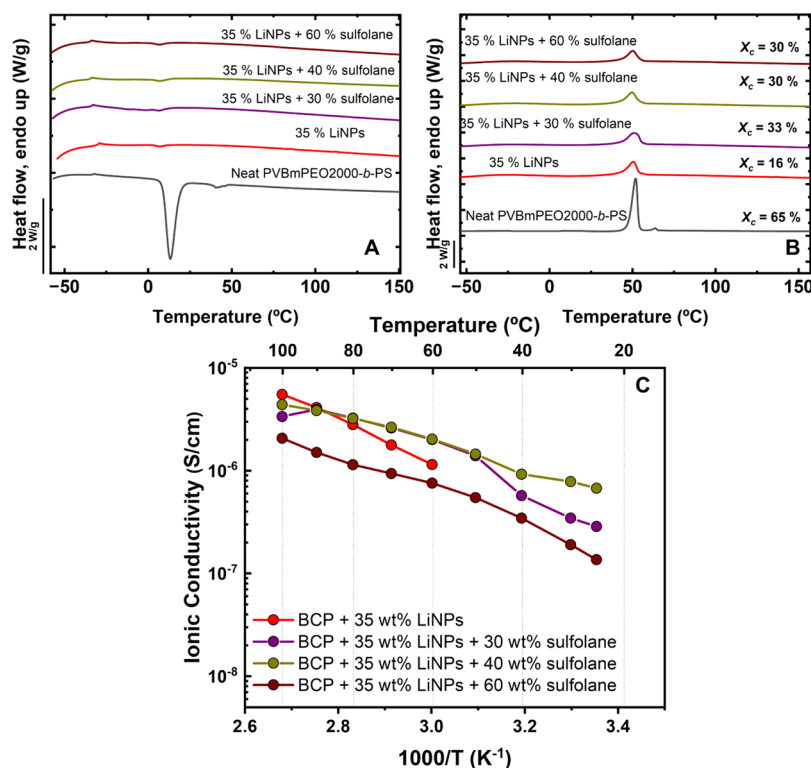


Figure 7. (A) DSC cooling scans from the melt and (B) subsequent heating scans of the neat BCP as well as the BCP with 35 wt % LiNPs and BCP with 35 wt % LiNPs containing 30, 40, and 60 wt % sulfolane; and (C) ionic conductivity results for PVBmPEO2000-*b*-PS with 35 wt % LiNPs and the BCP with 35 wt % LiNPs containing 30, 40, and 60 wt % sulfolane.

PC, or TEGDME) swells the PEO domains, which likely promotes the mobility of the PEO chains, helping with crystallization. The increase in crystallinity upon plasticization was previously reported by Yang et al.,²⁰ who studied PEO-PS-PEO copolymers. Although in their case, they attribute the increased crystallinity of the samples to the PEO cocrystallizing with the TEGDME plasticizer. Additionally, for our BCP, we believe the plasticizer affected only the PEO within the BCP (and not the LiNPs) because mixing the BCP with the plasticizer alone (without LiNPs) increases the crystallinity of the PEO (see the DSC cooling and heating runs in the [Supporting Information, Figure S8](#)).

4. CONCLUSIONS

In this work, we prepared hierarchical ion-conducting materials based on the self-assembly of polymer nanoparticles within a PVBmPEO2000-*b*-PS block copolymer. TEM and AFM images clearly show the lamellar morphology of the block copolymer and the ordering of the LiNPs within the PEO regions of the BCP. SAXS experiments further confirm that the BCP morphology is lamellar and remains unchanged upon the addition of the LiNPs and that the interlamellar distance increases due to their presence. DSC shows that increasing LiNP concentration decreases crystallinity, accompanied by an increase in ionic conductivity. Indeed, this work sheds light on the role of additives such as sulfolane, propylene carbonate, and tetraethylene glycol in PVBmPEO2000-*b*-PS block copolymer, evidencing their affinity for the PEO within the BCP rather than the LiNPs. As a result, we observe a slight increase in crystallinity, along with a minor change in ionic conductivity, following the addition of plasticizers. Notably, this strategy extends the operating temperature range of

the SPEs, achieving satisfactory ionic conductivities of 10^{-7} S/cm at 25 °C and 10^{-6} S/cm at 80 °C, while also ensuring the polymer electrolyte's film-forming ability and single-ion conduction. Indeed, preliminary electrochemical characterization revealed an extended electrochemical stability window (ESW) up to ≈ 4.5 V vs Li⁺/Li and a high lithium transference number of 0.93. These properties, along with the balance between crystallinity and extended ionic conductivity, highlight the potential of these polymer electrolytes for membrane thinning and further electrochemical optimization.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.6c01855>.

SAXS, TEM, and thermal characterization (DSC) results of BCP after annealing and solvent casting; SPE electrochemical characterization (ESW, transference number, and galvanostatic cycling); AFM, TEM, and SAXS images obtained from SPE characterization ([DOCX](#))

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Notes

The authors declare no competing financial interest.

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