

Safety-enhanced Polymer Electrolytes with High Ambient-temperature Lithium-ion Conductivity Based on ABA Triblock Copolymers

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 Electronic Supplementary Information

Abstract Liquid electrolytes used in lithium-ion batteries suffer from leakage, flammability, and lithium dendrites, making polymer electrolyte a potential alternative. Herein, a series of ABA triblock copolymers (ABA-*x*) containing a mesogen-jacketed liquid crystalline polymer (MJLCP) with a polynorbornene backbone as segment A and a second polynorbornene-based polymer having poly(ethylene oxide) (PEO) side chains as segment B were synthesized through tandem ring-opening metathesis polymerizations. The block copolymers can self-assemble into ordered morphologies at 200 °C. After doping of lithium salts and ionic liquid (IL), ABA-*x* self-assembles into cylindrical structures. The MJLCP segments with a high glass transition temperature and a stable liquid crystalline phase serve as physical crosslinking points, which significantly improve the mechanical performance of the polymer electrolytes. The ionic conductivity of ABA-*x*/lithium salt/IL is as high as 10^{-3} S·cm⁻¹ at ambient temperature owing to the high IL uptake and the continuous phase of conducting PEO domains. The relationship between ionic conductivity and temperature fits the Vogel-Tamman-Fulcher (VTF) equation. In addition, the electrolyte films are flame retardant owing to the addition of IL. The polymer electrolytes with good safety and high ambient-temperature ionic conductivity developed in this work are potentially useful in solid lithium-ion batteries.

Keywords ABA triblock copolymer; Polymer electrolyte; Ionic conductivity; Inflammability; Cylindrical structure

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INTRODUCTION

Lithium-ion battery (LIB), with high capacity and energy density, is the most used energy storage device nowadays.^[1,2] However, the nature of liquid electrolytes employed in LIB often causes plenty of problems such as leakage, flammability, and the formation of lithium dendrites.^[3–5] Solid polymer electrolytes (SPEs) are considered as an ideal substitution for liquid electrolytes because of their outstanding safety.^[6–11] As the most common SPE, poly(ethylene oxide) (PEO) suffers from crystallization and low ionic conductivity at ambient temperature.^[12–14] Many efforts have been devoted to allowing the suppression of PEO crystallinity and hence increasing the content of the amorphous phase, which is beneficial for ion transport.^[15–18] Among the various strategies, the employment of PEO-based block copolymers (BCPs) is a promising

solution.^[2,7,19–25] The net repulsion between the two or more segments of a BCP often induces microphase-separated structures with ordered morphologies and periodically spaced domains.^[26,27] The domain of PEO called as conducting domain plays a role in transporting lithium ions.^[28] On the contrary, the other component is always a hard polymer segment having a high glass transition temperature (T_g), which is supposed to provide high mechanical strength. Our group employed mesogen-jacketed liquid crystalline polymers (MJLCPs) in PEO-based BCPs to afford several high-temperature SPEs successfully.^[7,29] Balsara *et al.* have systematically studied the relationship between microphase separation and ionic conductivity of BCPs composed of polystyrene (PS) and PEO.^[20] They found that the ionic conductivities of SPEs with different self-assembled structures were distinct, and they used a morphology factor to describe the difference. For a spherical morphology with PEO as the dispersed phase, the morphology factor is 0 because no conducting pathways exist. For a cylindrical morphology with PEO as the dispersed phase, the morphology factor is 1/3 because ion transport only takes place in one-third of the directions. And the morphology factors are 2/3 and 1 for lamellar and bicontinuous morphologies,

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respectively. The morphology factor should always be 1 when the PEO domain is a continuous phase because the ions can transport in all directions. However, in most cases, the mechanical performances of these BCPs are unsatisfactory owing to their low molecular weights and weak chain entanglements.^[16] Chemical crosslinking is a natural thought to enhance the mechanical strength.^[30–32] However, the restriction on chain mobility by crosslinking will decrease the ionic conductivity severely.^[33] In addition, crosslinked polymers are usually insoluble and infusible, which increases the difficulty in processing. Therefore, polymer electrolytes based on physical crosslinking are attractive.

ABA triblock copolymers are widely used in traditional thermoplastic elastomers. Polymer components A are hard segments such as PS, and B segments are usually soft polymers such as polyisoprene. PS segments tend to aggregate together as physical crosslinking points owing to the immiscibility between the two segments, which simultaneously enhances the mechanical strength and maintains the processibility. Our group fabricated ion gels with high storage modulus with the incorporation of ABA triblock copolymers.^[34,35] Dobrynin and coworkers found that BCPs with linear-bottlebrush-linear structures were featured with tissue-relevant softness and enhanced firmness.^[36–38] On the microscopic scale, A segment with linear chains aggregates into one domain, while B segment with brush strands decreases the crosslinking density.^[39] Thus, ABA triblock copolymers showed rigid-while-flexible as well as soft-while-stiff properties.

In this work, a series of safety-enhanced polymer electrolytes with high ambient-temperature lithium-ion conductivity based on ABA triblock copolymers were prepared. The ABA triblock copolymers were synthesized through tandem ring-opening metathesis polymerization (ROMP). The segment A is PNBp,^[29] a kind of well-studied polynorbornene-based MJLCP with a high T_g and a stable liquid crystalline (LC) phase, and the segment B is comb-like PEO with a polynorbornene main chain. The ionic liquid (IL) doped in the polymer electrolytes is used to improve the ionic conductivity because IL usually has high ionic conductivity, low vapor pressure, fire-retardant property, and excellent high-temperature stability and is often used in gel electrolytes for LIBs.^[40–46] Due to the structural design of the ABA triblock copolymer which makes the conducting PEO domain be the continuous phase and the introduction of IL, the polymer electrolytes obtained have high safety and high ionic conductivity.

EXPERIMENTAL

Materials and Characterization

Dichloromethane (CH_2Cl_2) was purified with the solvent processing system (M. Braun, Inc.). 4,4'-Biphenol, 1-bromo-2-hexyldecane, *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride, acetic acid, 2-aminoterephthalic acid, polyethylene glycol monomethyl ether (PEGME, $M_n=400 \text{ g}\cdot\text{mol}^{-1}$), 1-ethyl-3-(3-(dimethylamino)-propyl) carbodiimide hydrochloride (EDC-HCl), 4-(dimethylamino) pyridine (DMAP), and other reagents were purchased from commercial sources and used as received without purification. ^1H -NMR and ^{13}C -NMR spectra were performed on a Bruker 400 MHz spectrometer. Number-averaged molecular weight (M_n) was obtained from size-exclusion chro-

matography (SEC) in THF by using a Waters 2410 instrument equipped with a Waters 2410 refractive index (RI) detector. Thermogravimetric analysis (TGA) examinations were recorded on a TA SDT 2960 instrument at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ under nitrogen. Differential scanning calorimetry (DSC) was performed on a TA DSC Q100 instrument on the first cooling and a subsequent heating process at a rate of $5 \text{ }^\circ\text{C}/\text{min}$ in a nitrogen atmosphere. Polarized light microscopy (PLM) was conducted on a Leitz Laborlux 12 microscope with a Leitz 350 hot stage. Small-angle X-ray scattering (SAXS) experiments were carried out on a Bruker Nanostar SAXS instrument using Cu K α radiation ($\lambda=0.154 \text{ nm}$ at 40 kV and 40 mA). The d -spacing (d) is obtained by $2\pi/q$, where the scattering vector q is defined as $q = 4\pi/\lambda \sin\theta$ (2θ is the scattering angle). Synchrotron-radiation SAXS experiments were conducted at Synchrotron X-ray Beamline 1W2A in the Beijing Synchrotron Radiation Facility (BSRF)^[47] and Synchrotron X-ray Beamline BL16B1 in the Shanghai Synchrotron Radiation Facility (SSRF). The tests of ionic conductivity were performed in an Autolab electrochemistry workstation with a voltage of 20 mV and a frequency from 1 Hz to 1000 kHz. Rheological experiments were conducted by using a MCR 301 rheometer with the frequency ranging from $0.1 \text{ rad}\cdot\text{s}^{-1}$ to $100 \text{ rad}\cdot\text{s}^{-1}$.

Synthesis of ABA Triblock Copolymers ABA-x

The synthetic route is shown in Scheme 1. The monomers NbPEO-400 and NbFp were synthesized according to our previous work,^[29] and the detailed process is described in the electronic supplementary information (ESI). The ABA triblock copolymers were synthesized with tandem ROMP. The synthesis of ABA-3 is described below as an example. NbFp (20 equiv., 126 mg, 0.113 mmol) in 0.5 mL of CH_2Cl_2 was added into a Schleck tube. The tube was degassed with three freeze-pump-purge-thaw cycles using high-purity nitrogen. The Grubbs catalyst (the third generation, 1 equiv., 5.0 mg, $5.7 \mu\text{mol}$) was added quickly, followed by another three pump-purge cycles. The solution was stirred at ambient temperature for 15 min, then NbPEO-400 (50 equiv., 300 mg, 0.283 mmol) in 1.0 mL of CH_2Cl_2 was injected and stirred for another 15 min. Trace samples were taken out from the mixture to perform SEC examination. NbFp (20 equiv., 126 mg, 0.113 mmol) in 0.5 mL of CH_2Cl_2 was injected to the solution again. After 2 h, 0.1 mL of ethyl vinyl ether was added to quench the reaction. The mixture was passed through a neutral alumina column to remove the Grubbs catalyst, and then it was precipitated in 200 mL of petroleum ether to obtain a white solid.

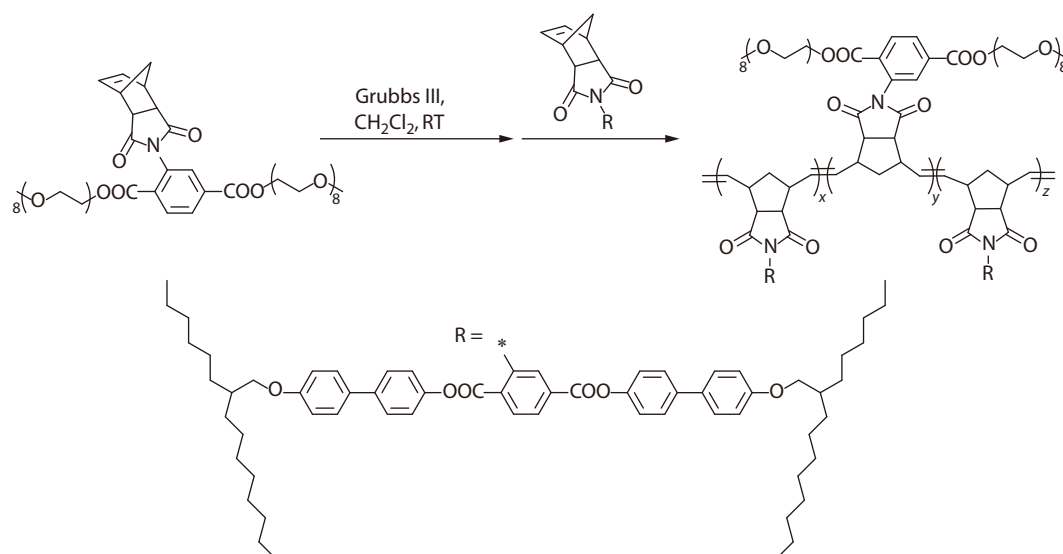
Doping of Lithium Salt and IL

The ABA triblock copolymer (20.0 mg) and an appropriate amount of lithium bistrifluoromethanesulfonimide (LiTFSI) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIMTFSI) were dissolved in 2 mL of chloroform (CHCl_3), and the mixture was stirred at ambient temperature for 24 h. After the solvent evaporated, the residue was dried at $80 \text{ }^\circ\text{C}$ in vacuum for 12 h to remove the residual solvent.

RESULTS AND DISCUSSION

Synthesis of ABA-x

A series of ABA triblock copolymers with different compositions were synthesized with tandem ROMP. ROMP were often used in



the polymerization of monomers with large volumes like NbFp and NbPEO-400 in this work.^[48] In the chemical structure of the ABA triblock copolymer, A segment is composed of a MJLCP with a polynorbornene backbone and B segment is a polynorbornene-based polymer having PEO side chains. The microphase separation between the A and B segments leads the aggregated A segments to behave like physical crosslinking points. Owing to the physical crosslinking of A segments, which is beneficial to improve the mechanical strength of the SPE, the content of PEO could be further increased without losing the self-supporting capability of the SPE films compared with the diblock copolymer we used in our previous work,^[29] and the high content of PEO in SPE is very important for obtaining excellent electrochemical properties.

The target ABA-3 BCP sample is pure without any residual monomers, diblock copolymers, or homopolymers, as proven by the SEC trace (Fig. 1). Fig. 1(a) shows SEC curves at different reaction time. The curve at right is the SEC trace of the homopolymer PNBfP₁₃. The middle curve shows the SEC curve of the diblock copolymer PNBfP₁₃-b-PNBPEO₄₄, and the left one shows that of the ABA triblock copolymer ABA-3. There is only one symmetric peak in the curves of PNBfP₁₃-b-PNBPEO₄₄ and ABA-3, demonstrating that the polymerization reaction is complete. The detailed information of ABA-*x* samples is shown in Table 1. The mass fractions of PEO in ABA-*x*, denoted as w_{EO} , are determined by the ratios of peak areas of hydrogens in ¹H-NMR spectra (Fig. S1 in ESI).

Thermal Properties of ABA-x/LiTFSI/IL

The thermal stability of ABA-*x* was examined by TGA. The 5% weight loss temperatures of all polymer samples are over 300 °C, proving their excellent thermal stabilities. The DSC thermograms of ABA-3 and the complexes of ABA-3 with LiTFSI and IL (ABA-3/LiTFSI/IL, the mass fraction of IL is 100%) are shown in Fig. 2. The crystallization and melting peaks of PEO are almost invisible in the cooling and heating curves, and a sharp peak at 216 °C appears during heating, which should be attributed to the phase transition from the LC phase to the

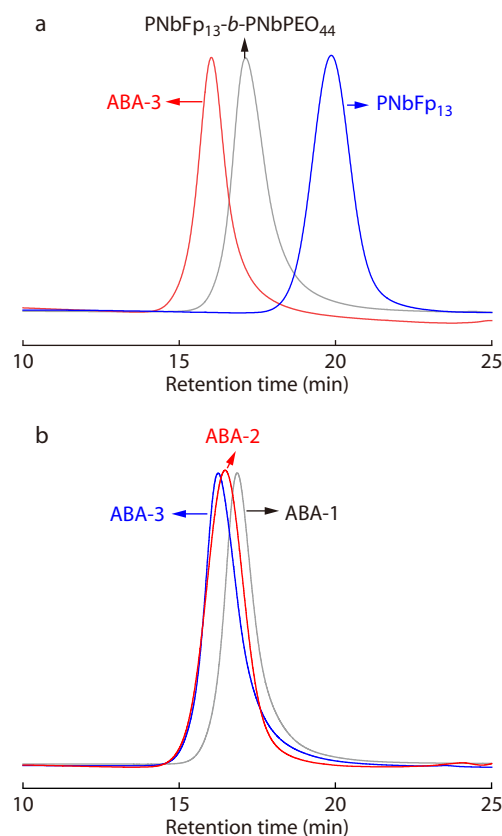
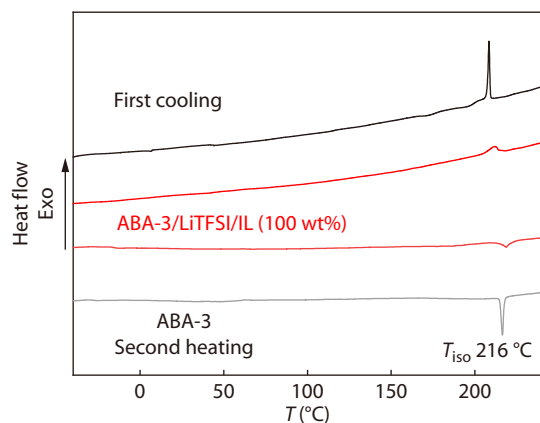


Fig. 1 SEC traces of ABA triblock copolymer ABA-3, diblock copolymer PNBfP₁₃-*b*-PNbPEO₄₄, and homopolymer PNBfP₁₃ (a) and those of ABA triblock copolymers ABA-1, ABA-2, and ABA-3 (b).

Table 1 Molecular characteristics of ABA-1, ABA-2, and ABA-3.

Sample	$M_n^a \times 10^{-3} \text{ (g} \cdot \text{mol}^{-1})$	D_M^a	$w_{EO}^b \text{ (%)}$	$T_d^c \text{ (}^\circ\text{C)}$
ABA-1	65	1.27	38	332
ABA-2	68	1.33	40	335
ABA-3	76	1.30	43	330

^a Determined from SEC results; ^b Determined from $^1\text{H-NMR}$ results; ^c 5% Weight loss temperature (T_d), determined by TGA at a heating rate of $10^\circ\text{C} \cdot \text{min}^{-1}$ under nitrogen.

**Fig. 2** The first-cooling and the second-heating DSC thermograms of ABA-3 and ABA-3/LiTFSI/IL (100 wt%) at a rate of $10^\circ\text{C} \cdot \text{min}^{-1}$.

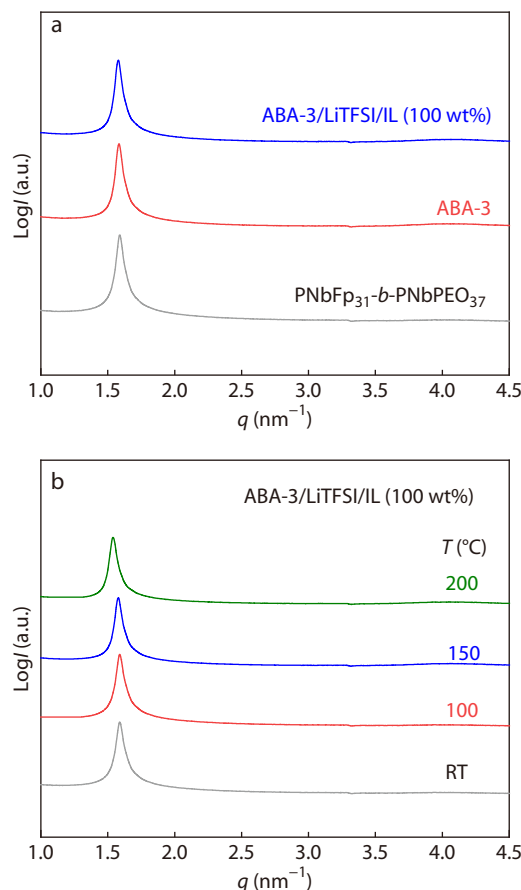
phase. The DSC results of ABA-1 and ABA-2 are similar to those of ABA-3.

LC Properties of ABA-*x*/LiTFSI/IL

The LC properties of ABA-3/LiTFSI/IL were studied by one-dimensional (1D) WAXS. The WAXS profiles of PNB Fp_{31} - b -PNbPEO $_{37}$, ABA-3, and ABA-3/LiTFSI/IL (100 wt%) at ambient temperature are shown in Fig. 3(a). The sharp peaks at $q = 1.60 \text{ nm}^{-1}$ (and the corresponding d -spacing is 3.93 nm) are attributed to the LC structures. The q value and intensity of the peak does not change with the doping of LiTFSI or IL probably because LiTFSI and IL are more compatible with polar ether groups so that they tend to stay in the PEO domain. Variable-temperature WAXS profiles in Fig. 3(b) illustrate that the LC structure of ABA-3/LiTFSI/IL (100 wt%) is stable even at a high temperature of 200°C .

Microphase Separation Induced by Doping of LiTFSI and IL

The self-assembling behaviors of ABA-*x*/LiTFSI/IL were also investigated by SAXS. According to our previous studies,^[29] the introduction of lithium salts and their contents affect the self-assembling structures of the BCPs. The hexagonally packed cylindrical (HEX) structure was obtained by controlling the volume fraction of the PEO segment and the content of lithium salt. The amount of IL doped was as high as 175% (W/W) without severe decrease in mechanical strength, attributed to the physically crosslinked structure. The SAXS profiles of ABA-3/LiTFSI/IL with different contents of IL are shown in Fig. 4(a). There are several diffraction peaks in the low-angle region, and the ratio of their scattering vectors is $1:3^{1/2}:2:7^{1/2}$, indicating a HEX structure. With the amount of IL doped increasing from 75 wt% to 175 wt%, the position of the primary diffraction peak shifts from 0.213 nm^{-1} to 0.206 nm^{-1} (with the d -spacing

**Fig. 3** 1D WAXS profiles of PNB Fp_{31} - b -PNbPEO $_{37}$, ABA-3, and ABA-3/LiTFSI/IL (100 wt%) at ambient temperature (a) and those of ABA-3/LiTFSI/IL at different temperatures (b).

changing from 29.5 nm to 30.5 nm), which is mainly owing to the larger volume of the PEO/LiTFSI/IL phase with more IL. High-temperature stability of the HEX structure was investigated with variable-temperature SAXS (Fig. 4b). The intensities of the diffraction peaks and the scattering vector ratio at 200°C are almost identical to the ones at ambient temperature, indicating the outstanding high-temperature stability of ABA-3/LiTFSI/IL. Such a high stability may be attributed to the stable LC structure of the MJLCP segment at high temperatures because the T_{iso} of most MJLCP is very high. The microphase separation behaviors of ABA-1/LiTFSI/IL and ABA-2/LiTFSI/IL are similar to those of ABA-3/LiTFSI/IL, and the details are shown in Figs. S2 and S3 in ESI. The self-assembling behavior of ABA-*x*/LiTFSI/IL is illustrated in Fig. 5. Although the HEX structures in this work are not well oriented and many grain boundaries are likely to exist to hinder the ionic conduction, the high content of PEO in the ABA-*x* sample makes it the continuous phase, and thus lithium ions can migrate in all three dimensions.^[20]

Ionic Conductivity of ABA-*x*/LiTFSI/IL

Electrical impedance spectrum measurements were used to investigate the ionic conductivities (σ 's) of ABA-*x*/LiTFSI/IL samples with different contents of lithium salt and IL at ambient temperature. Fig. S4 (in ESI) shows the σ values of ABA-3/LiTFSI/IL (the content of IL is 150 wt%) with $[\text{Li}^+]/[\text{EO}]$ of 1/20, 1/10, and 1/5. A maximum σ value is obtained when $[\text{Li}^+]/[\text{EO}]$ is

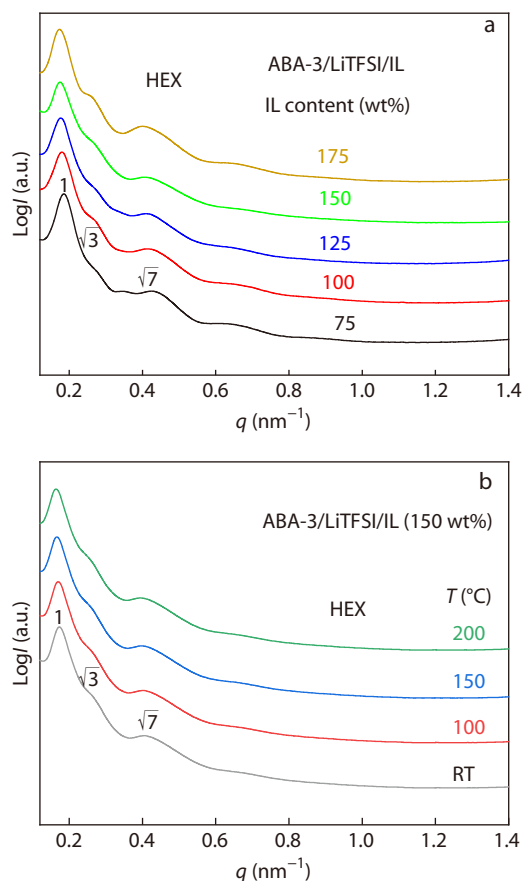


Fig. 4 SAXS profiles of ABA-3/LiTFSI/IL with different IL contents (a) and those of ABA-3/LiTFSI/IL (150 wt%) at different temperatures (b).

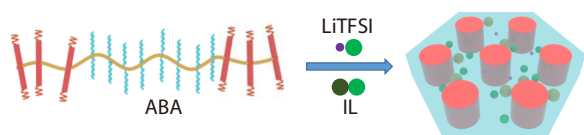


Fig. 5 Schematic illustration of the LiTFSI and IL-induced microphase separation of the ABA triblock copolymer.

1/10. Thus, the doping amount of lithium salt in the subsequent research was fixed as $[Li^+]/[EO]=1/10$. The IL dependency of ion conductivities of ABA- x /LiTFSI/IL ($x=1, 2, 3$) is shown in Fig. 6(a). The σ value is linearly enhanced with the increase of the IL content when it is below 150 wt% whereas the enhancement is limited when the IL content is further increased. Considering the high IL content may reduce the mechanical stability, the IL content of 150 wt% is chosen as be the best value. Even though the IL content is only 150 wt%, the ionic conductivity reaches up to 10^{-3} S·cm $^{-1}$, which is higher than the values of most other polymer electrolytes.

The ionic conductivity of ABA-3/LiTFSI/IL (150 wt%) at different temperatures is shown in Fig. 6(b). The σ value increases with increasing temperature between -25 and 200 °C, which is in agreement with the higher lithium ion mobility at higher temperatures. In addition, the σ values at different temperatures can be fitted with the Vogel-Tamman-Fulcher (VTF) equation, demonstrating the high-temperature stability

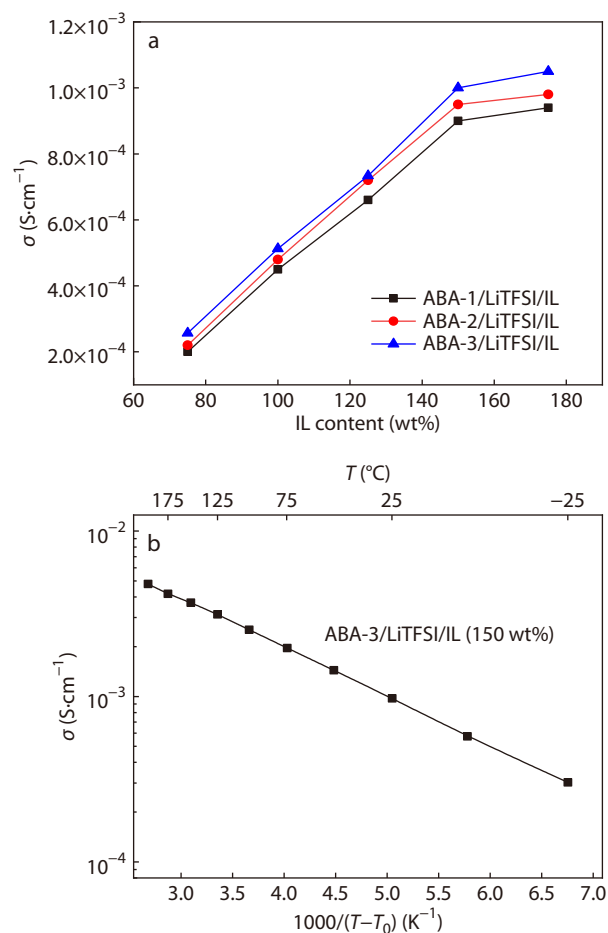


Fig. 6 Ionic conductivity of ABA- x /LiTFSI/IL ($x=1, 2, 3$) with different IL contents (a) and that of ABA-3/LiTFSI/IL (150 wt%) at different temperatures (b).

of ABA-3/LiTFSI/IL. Furthermore, the ionic conductivity is above 10^{-4} S·cm $^{-1}$ even when the temperature is -25 °C, which is uncommon because many polymer electrolytes crystallize at such a low temperature and their ionic conductivities would severely decrease.

Mechanical Properties of ABA- x /LiTFSI/IL

Shear rheological experiments were conducted to investigate the rheological properties of ABA- x /LiTFSI/IL. The result at ambient temperature is shown in Fig. 7(a). The values of storage modulus (G') and loss modulus (G'') are comparable to those of the BCP with an analogous structure in our previous work.^[29] With the consideration that the higher IL content in the triblock copolymer electrolyte should reduce the modulus, the physical crosslinking of the ABA structure plays an important role in maintaining the mechanical strength. In addition, the value of G' is always higher than G'' from -25 °C to 200 °C in the variable-temperature rheological experiments with a shear rate of 1 rad·s $^{-1}$ (Fig. 7b), demonstrating the excellent mechanical stability compared with many gel electrolytes having high σ values. Tensile tests were performed to study the mechanical properties of ABA- x /LiTFSI/IL. The stress-strain curves in Fig. S5 (in ESI) shows the Young's modulus and elongation at break of ABA-3/LiTFSI/IL (100 wt%) are about 2.8 MPa and 20%,

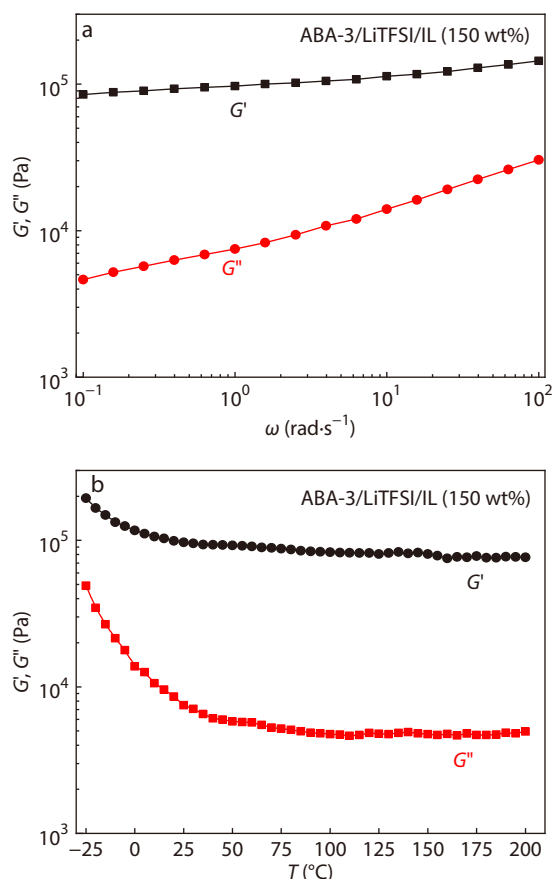


Fig. 7 Shear rheological profiles of ABA-3/LiTFSI/IL (150 wt%) at different frequencies (a) and different temperatures (b).

respectively, and a slight change occurs when the amount of IL doped is increased to 150 wt%.

Inflammability of ABA-*x*/LiTFSI/IL

Flammability of liquid electrolytes is thought to be one of the biggest safety issues for commercial lithium-ion batteries. Herein, the inflammability of ABA-3/LiTFSI/IL (150 wt%) electrolyte was evaluated by ignition upon flame. Figs. 8(a) and 8(b) show the polymer film before and after contact with flame. The polymer film is still stable even after 8 s of burning (Fig. 8c). Furthermore, the fire dies out quickly after the flame is removed, as shown in Fig. 8(d) and Movie S1 (in ESI). Low flammability of several other SPEs have been reported in the literature.^[49–51] Tu and his coworkers reported a porous polyamide skeleton-reinforced SPE which was flame-retardant with low flammability. However, the SPE film was only in contact with fire instead of being burned. So the ABA SPEs in this work were more flame-retardant and safer.

The ABA-*x*/LiTFSI/IL triblock copolymer electrolytes exhibit impressive improvements compared with the diblock copolymer electrolytes in our previous study. The improvements can be attributed to the following reasons. On the one hand, by introducing physical crosslinking points of A segments, the IL content can be increased to 150 wt%, with the ionic conductivity improved to be 10^{-3} $\text{S}\cdot\text{cm}^{-1}$. And the physical crosslinking provides the polymer electrolytes with stretchability which was not observed in the diblock copolymer electro-

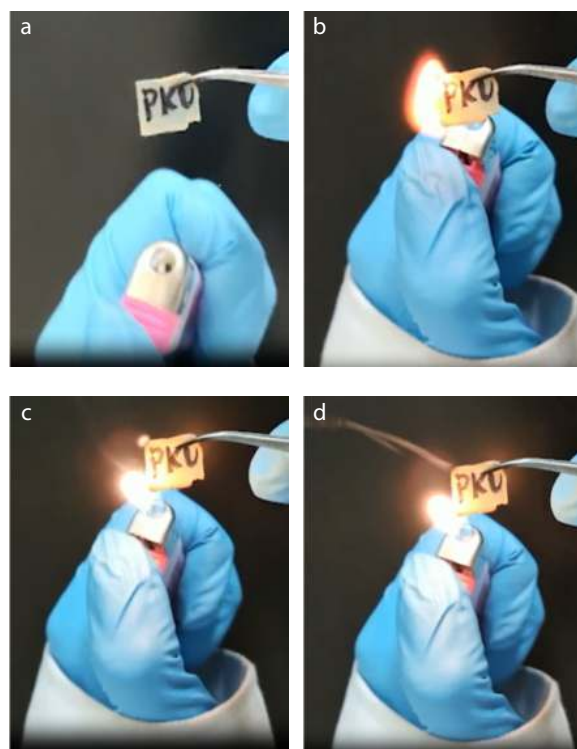


Fig. 8 Inflammability tests of a ABA-3/LiTFSI/IL (150 wt%) film.

lytes. On the other hand, the high content of IL in the electrolytes makes the electrolyte films flame retardant. It has been reported that batteries based on polymer electrolyte with ionic liquid showed excellent cycling performance.^[52] Therefore, solid-state lithium-ion batteries based on ABA SPE were also believed to have outstanding electrochemical performance.

CONCLUSIONS

A series of ABA triblock copolymers were synthesized through tandem ROMP. Their complexes with LiTFSI and IL self-assemble into HEX nanostructures that are stable from ambient temperature to 200 $^{\circ}\text{C}$. The MJLCP segment A in the triblock copolymers improves the mechanical performance of the polymer electrolytes because the MJLCP segments aggregate to serve as physical crosslinking points. The PEO-containing domain is the continuous phase, which allows ion conduction in all directions. The IL doped in the triblock copolymers significantly increases the ionic conductivity at ambient temperature, and the highest σ value reaches 10^{-3} $\text{S}\cdot\text{cm}^{-1}$ which is higher than those of most other polymer electrolytes. The mechanical strength of the ABA-*x*/LiTFSI/IL polymer electrolytes is enhanced because of the ABA structure. Compared with AB diblock copolymers having similar chemical compositions investigated in our previous study,^[29] the ionic conductivity and mechanical performance of SPE based on ABA triblock copolymers were highly improved. The enhancement of the performance is a result of the unique design of the chemical structure of ABA triblock copolymer. In addition, the polymer electrolytes are flame retardant and can self-extinguish after the flame is removed. These polymer electrolytes based on ABA

triblock copolymers with high safety and ionic conductivity are potentially useful in solid-state lithium ion batteries and flexible lithium ion batteries.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

The following files are available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-021-2648-2>. Synthesis of NbPEO-400 and NbFp, ^1H -NMR spectrum of ABA-3, ambient and variable-temperature SAXS profiles of ABA-1/LiTFSI/IL and ABA-2/LiTFSI/IL, ionic conductivity of ABA-3/LiTFSI/IL with different amounts of lithium salt, and tensile curves of ABA-3/LiTFSI/IL (PDF). Video of inflammability tests of the polymer electrolyte film (MP4).

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