

Effects of Ionic Liquids on Piezoelectric Properties of Electrospun Poly(L-lactic acid) Nanofiber Membranes

Xiaoxia Gu, Meng Cui,* Bin Wang, Guyue Liu, Jing Zhang, Rui Wang, and Xiuqin Zhang*

Cite This: *ACS Omega* 2024, 9, 4957–4965

Read Online

ACCESS |



Metrics & More

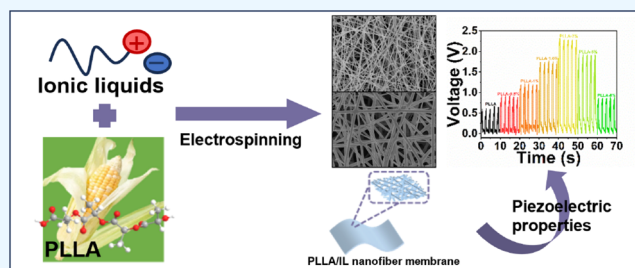


Article Recommendations



Supporting Information

ABSTRACT: The development of environmentally friendly, degradable piezoelectric materials is of great significance for the environment. Poly(L-lactic acid) (PLLA) is a promising piezoelectric material as a degradable material. Here, we have introduced a series of ionic liquids (ILs) into PLLA spinning solution, and the PLLA/IL composite nanofiber membranes are prepared by electrospinning method. When the conductivity of the spinning solution is below $400 \mu\text{S}\cdot\text{cm}^{-1}$, the addition of ILs, especially [EMIm][PF₆], can significantly improve the morphology and piezoelectric properties of the PLLA/IL composite nanofiber membrane with the output voltage of 2.3 V under the pressure of 5 N, which is 4 times that of the PLLA nanofiber membrane. The improvement of the piezoelectric properties of PLLA/IL nanofiber membrane may be due to the high dipole moment generated by the C=O dipole after the interaction between the O atom in C=O on the PLLA molecular chain and the [EMIm]⁺ cation in the IL. This work has elucidated the effects of ILs on the properties of spinning solution and the piezoelectric properties of PLLA, which can provide a theoretical basis for the selection of the preparation system of piezoelectric polymer and inspire the development of environmentally friendly flexible piezoelectric materials.



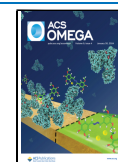
1. INTRODUCTION

With the development of the smart wearable field, flexible materials suitable for wearable electronic devices have attracted much attention. Piezoelectric materials can convert mechanical energy into electrical energy for sensors, actuators, and energy harvesting.^{1–3} Although the piezoelectric coefficient of inorganic piezoelectric materials represented by piezoelectric ceramics is high, the inorganic piezoelectric materials are generally hard and brittle, and it is difficult to bend or process into a specific shape,⁴ which limits their application in flexible electronic devices.^{5–7} Organic piezoelectric materials such as polyvinylidene fluoride (PVDF), polyvinyl chloride, polyacrylonitrile (PAN), and other polymers have good piezoelectric properties and bending tensile properties, which have been widely studied in recent years.^{8–10} They can maintain stable electrical signal output under deformation and have application potential in flexible electronic devices.^{9–11} The piezoelectricity of polymers comes from the dipoles in their molecular structures. Whether semicrystalline polymers or amorphous polymers, polymers with dipoles can exhibit certain piezoelectric properties.¹² However, the preparation of most piezoelectric polymers relies on traditional fossil fuels and is difficult to degrade, causing serious damage to the environment. Therefore, the development of environmentally friendly degradable piezoelectric materials for smart wearable devices is of great significance.

Poly(L-lactic acid) (PLLA) is a degradable polymer prepared from renewable resources such as starch and glucose,

which can effectively solve the nonrenewable and non-degradable problems of petroleum-based polymer resources.¹³ The reason why PLLA has a piezoelectric effect is because its molecule contains C=O dipoles, the positive and negative centers of the dipole do not overlap, the C atom in C=O is positively charged, and the O atom is negatively charged, resulting in a potential difference. With the C=O dipoles on the molecular chain of PLLA, the piezoelectric properties will be enhanced after polarization treatment.^{14,15} Electrospinning technology is widely used in the field of piezoelectricity. The electric field applied in the electrospinning process can polarize the material, which make the material have good piezoelectric properties without postprocessing.¹⁶ In addition, electrospinning technology can also realize the combination of various materials to promote the piezoelectric properties. For example, the piezoelectric nanogenerator prepared by electrospinning of PLLA and vitamin B₂ had a maximum power density of 75.68 mW/cm³, which was about 28.7 times that of the PLLA nanogenerator.¹⁷ CO₂-based polyurea (PU) and PLLA were compounded in our previous work, and the voltage

Received: November 5, 2023
Revised: December 14, 2023
Accepted: January 8, 2024
Published: January 20, 2024



of the PU/PLLA piezoelectric sensor was 15 times that of the PLLA piezoelectric sensor.¹⁸ Although there have been some studies on the use of electrospinning to combine PLLA with organics, the effect of spinning solution properties on piezoelectric properties of PLLA has not been reported before.

Ionic liquid (IL) is an organic salt composed of ion pairs, which is usually liquid at room temperature,¹⁹ and can be widely used in many fields, such as green catalysis, solar cells, and environmental pollution control.^{20–22} Because of the advantages of low volatility, low vapor pressure, wide electrochemical window, high thermal stability, and high ionic conductivity,^{23–27} IL can be used as an ideal filler in electrospinning polymer solution and effectively improve the sensing performance of piezoelectric sensors. Shi et al. regulated the structure and properties of PAN by adding a small amount of 1-allyl-3-butylimidazolium tetrafluoroborate and FeCl₃·6H₂O, which greatly improved the piezoelectric properties of the composite nanofibers.²⁸ Varposhti et al. added ILs to PVDF nanofibers to increase the β -phase content of the polymer, thereby increasing the piezoelectric response of the polymer. Compared with pure nanofibers, the output voltage and power density were increased by 186.9% and 275%, respectively.²⁹

In this work, a series of ILs were introduced into PLLA spinning solution, and the PLLA/IL composite nanofiber membranes were prepared by electrospinning method. The fiber diameter of PLLA could be reduced by the addition of IL. The PLLA/1-ethyl-3-methylimidazolium hexafluorophosphate ([EMIm][PF₆]) composite nanofiber membrane had the best piezoelectric performance, and the voltage was 2.3 V, which was 4 times that of the PLLA nanofiber membrane. This work has elucidated the effects of ILs on the properties of spinning solution and the piezoelectric properties of PLLA, which have filled the gap in related fields and provided a theoretical basis for the selection of the preparation system of the piezoelectric polymer.

2. EXPERIMENTAL SECTION

2.1. Materials. Poly(L-lactic acid) (PLLA) (REVODE190) was purchased from Zhejiang Haizheng Biomaterials Co., Ltd. Hexafluoroisopropanol (HFIP, 99%) was purchased from Beijing Inno Chem Science & Technology Co., Ltd. Ethanol, dichloromethane (DCM), and sodium hydroxide (NaOH) were all A. R. grade and purchased from Beijing Chemical Reagent Co., Ltd. 1-Ethyl-3-methylimidazolium hexafluorophosphate ([EMIm][PF₆], 99%), 1-ethyl-3-methylimidazolium chloride ([EMIm][Cl], 99%), 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIm][BF₄], 99%), 1-ethyl-3-methylimidazolium hydrogensulfate ([EMIm][HSO₄], 99%), 1-ethyl-3-methylimidazolium acetate ([EMIm][OAc], 99%), 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide ([EMIm][NTf₂], 99%), tetraethylammonium hexafluorophosphate ([N₂₂₂₂][PF₆], 99%), N-ethylpyridinium hexafluorophosphate ([EPy][PF₆], 99%), N-butylpyridinium hexafluorophosphate ([BPy][PF₆], 99%), 1,3-dimethylimidazolium hexafluorophosphate ([MMIm][PF₆], 99%), 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm][PF₆], 99%), and 1-octyl-3-methylimidazolium hexafluorophosphate ([OMIm][PF₆], 99%) were purchased from Qingdao Aolike New Materials Technology Co., Ltd. Deionized water was provided by laboratory. All materials and chemicals were used as received.

2.2. Preparation of Different PLLA/IL Nanofiber Membranes. PLLA (1.6 g) and different kinds of ILs (0.08 g) were loaded into a triangular flask and dissolved in 10 mL of mixed solvent of DCM and HFIP ($V_{\text{DCM}}/V_{\text{HFIP}} = 7/3$). After stirred for 2 h at 30 °C, a series of different proportions of PLLA/IL composite spinning solution was obtained. High-voltage electrospinning machine (TL-Pro-BM) was used to spray the above spinning solution under the same spinning conditions on aluminum foil to prepare PLLA/IL nanofiber membranes. The detailed spinning conditions were set as follows. The speed of collecting the mandrel and the solution flow rate were set at 100 r·min⁻¹ and 0.1 mL·h⁻¹, respectively. The voltage was set at 18 kV, and the spinning time was 10 h. The distance between the needle and the counter electrode was 15 cm.

The PLLA nanofiber membrane was prepared for comparison. However, because the PLLA spinning solution and PLLA/IL composite spinning solution have different solution properties, the spinning conditions which were suitable for the PLLA spinning solution were set as follows. The speed of collecting mandrel and the solution flow rate were set at 100 r·min⁻¹ and 1 mL·h⁻¹, respectively. The voltage was set at 18 kV, and the spinning time was 1 h. The distance between the needle and the counter electrode was 15 cm.

2.3. Preparation of PLLA/[EMIm][PF₆] Composite Nanofiber Membranes with Different [EMIm][PF₆] Content. Different proportions of PLLA/[EMIm][PF₆] composite spinning solution were prepared by using 1.6 g of PLLA and a certain amount of [EMIm][PF₆] (based on the mass fraction of PLLA, 0.5, 1, 1.5, 2, 5, and 8 wt %) according to the above experimental method.

The PLLA/[EMIm][PF₆] composite nanofiber membranes were prepared on aluminum foil by electrospinning under the same spinning conditions. The speed of collecting mandrel and the solution flow rate were set at 100 r·min⁻¹ and 0.1 mL·h⁻¹, respectively. The voltage was set at 18 kV, and the spinning time was 10 h. The distance between the needle and the counter electrode was 15 cm. The PLLA/[EMIm][PF₆] composite nanofiber membranes were named PLLA-0.5%, PLLA-1%, PLLA-1.5%, PLLA-2%, PLLA-5%, and PLLA-8%.

2.4. Characterization. The conductivities of all different formulations of spinning solution were tested by a conductivity meter (DDS-11A, Shanghai Yidian Scientific Instrument Co., Ltd.) to characterize the properties of the spinning solutions. The morphology of the nanofiber membrane was characterized by field emission scanning electron microscopy (SEM, JSM-7500F, Japan Electronics Co., Ltd.). X-ray diffraction (XRD, D8 Discover, Bruker) and Fourier transform infrared spectroscopy (FTIR, Thermo Nicolet iS10, Thermo Fisher Scientific) were used to characterize the structure of the nanofiber membrane. The thermal stability of nanofiber membrane was tested by a thermogravimetric analyzer (TG, 209 F1, Netzsch), and the heating rate was 10 °C/min. The hydrophobicity of the nanofiber membrane was measured by an optical contact angle measuring instrument (OCA20, Germany Dataphysics Instrument Co., Ltd.). The nanofiber membrane was tested by a differential scanning calorimeter (DSC, Q-2000, TA Instruments). The heating and cooling rate was 10 °C/min, and the temperature range was 25–250 °C.

2.5. Test of Piezoelectric Property. The thickness of all the nanofiber membranes used for the test was about 15 μm . Aluminum foil was used as the electrode on both sides of the membrane, and then, two copper strips were led out from the

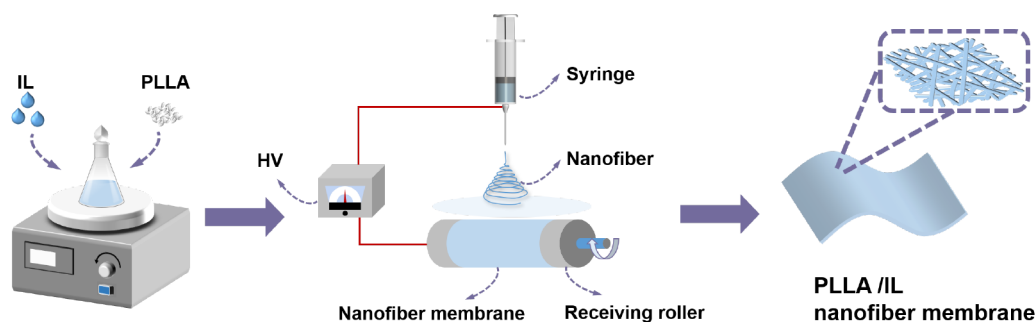


Figure 1. Preparation of the PLLA/IL nanofiber membrane.

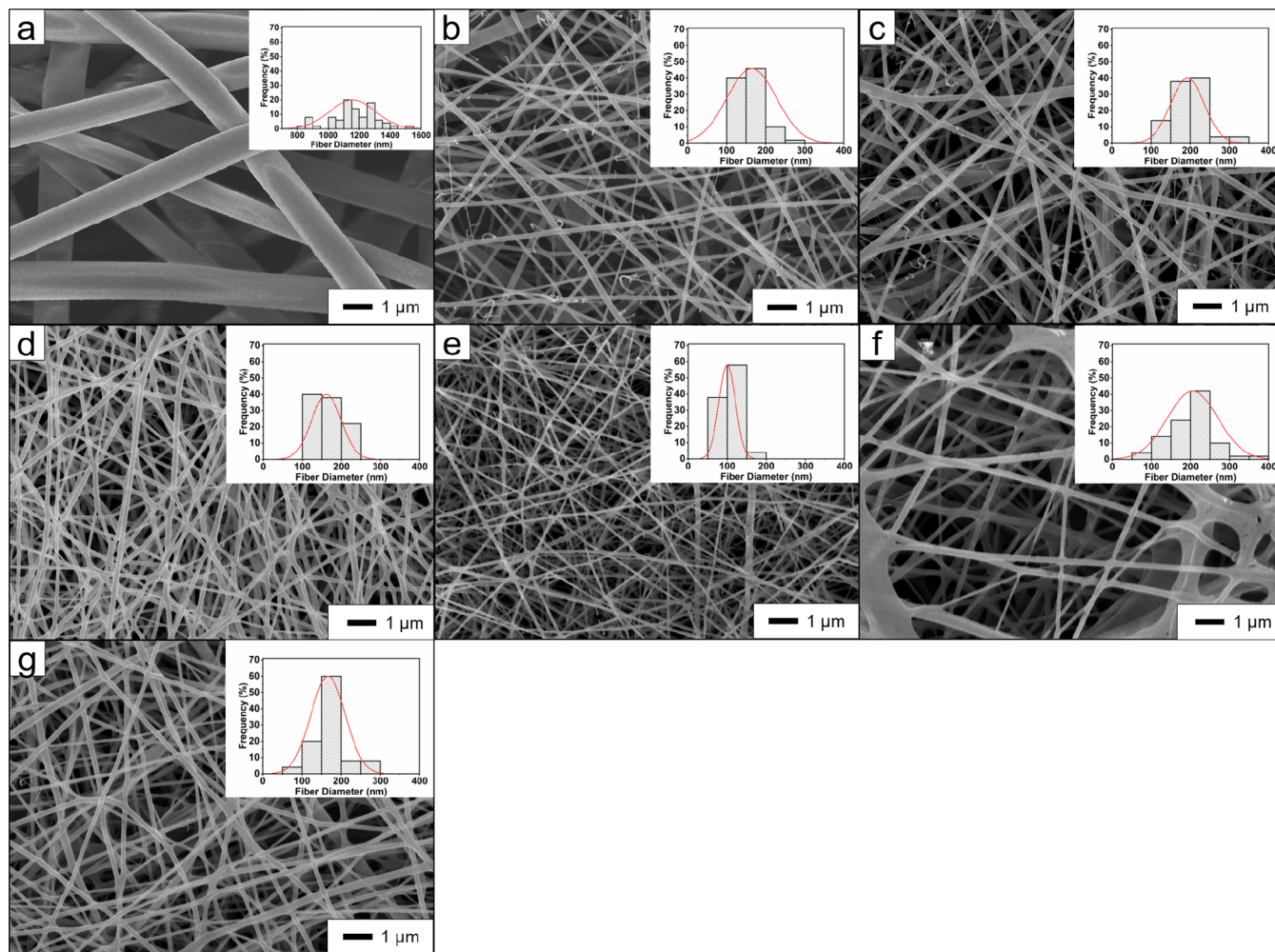


Figure 2. SEM images and fiber diameter distribution of nanofiber membranes: (a) PLLA; (b) PLLA/[EMIm][Cl]; (c) PLLA/[EMIm][BF₄]; (d) PLLA/[EMIm][PF₆]; (e) PLLA/[EMIm][HSO₄]; (f) PLLA/[EMIm][OAc]; and (g) PLLA/[EMIm][NTf₂].

electrode and connected with the wire. The device described above was encapsulated with transparent tape. The linear motor was used to provide a constant pressure to the membranes, and an electrometer (Keithley 6514) was used to collect the electrical signals generated from the nanofiber membranes.

3. RESULTS AND DISCUSSION

PLLA/IL nanofiber membranes were prepared by electrospinning technology, as shown in Figure 1. In order to analyze the effects of different ILs on the electrospinning process of PLLA, we used SEM to characterize the morphology of PLLA/

IL nanofiber membranes and compared it with the PLLA nanofiber membrane. As shown in Figure 2, the effects of [EMIm]⁺ series ILs on PLLA nanofibers were analyzed. It could be seen that the fiber diameter distribution of PLLA nanofiber membranes was wide and the fiber diameter was large, mainly distributed at 1000–1300 nm (Figure 2a; Table S1). The addition of [EMIm]⁺ series ILs reduced the diameter and the diameter distribution range of the nanofibers (Figure 2b–g; Table S1). However, the addition of [EMIm][Cl] and [EMIm][BF₄] made the nanofibers flocculent (Figure 2b,c), while the addition of [EMIm][OAc] made the nanofibers seriously adherent (Figure 2f).

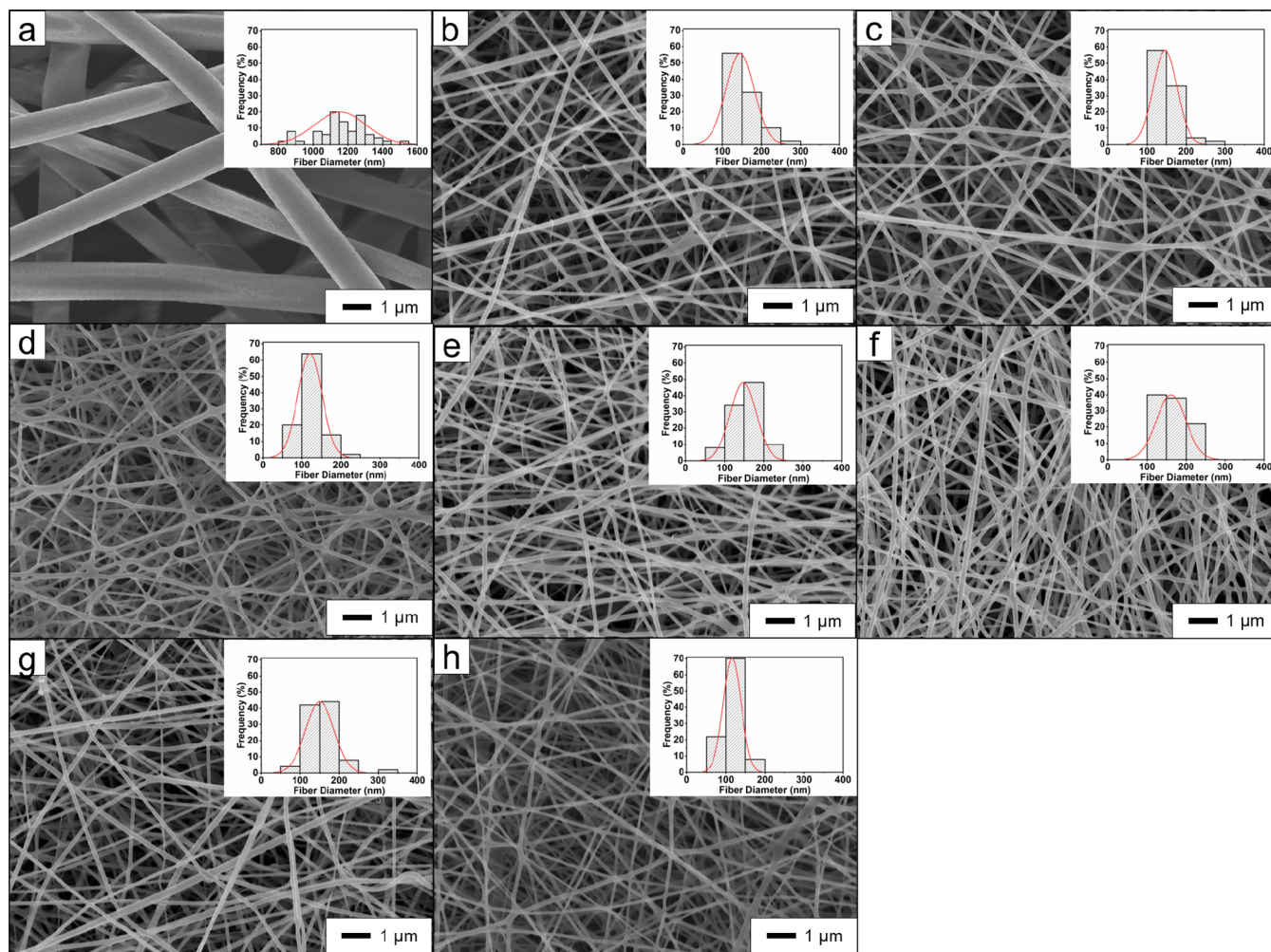


Figure 3. SEM images and fiber diameter distribution of nanofiber membranes: (a) PLLA; (b) PLLA/[N₂₂₂₂][PF₆]; (c) PLLA/[EPy][PF₆]; (d) PLLA/[BPy][PF₆]; (e) PLLA/[MMIm][PF₆]; (f) PLLA/[EMIm][PF₆]; (g) PLLA/[BMIm][PF₆]; (h) PLLA/[OMIm][PF₆].

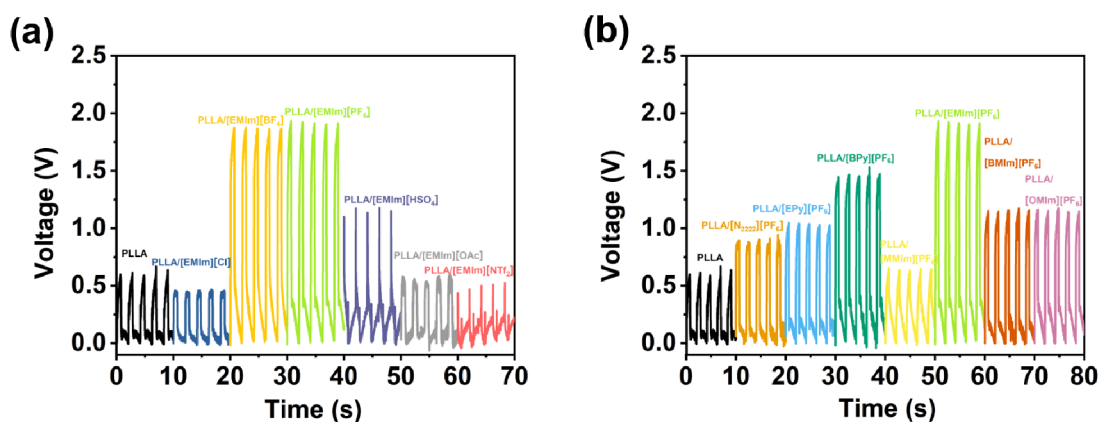


Figure 4. Piezoelectric test results of nanofiber membranes with different types of ILs: (a) [EMIm]⁺ series ILs; (b) [PF₆]⁻ series ILs.

The effects of the [PF₆]⁻ series ILs on the morphology of PLLA nanofibers were also analyzed by SEM (Figure 3). Compared with the PLLA nanofiber membrane, the addition of [PF₆]⁻ series ILs also reduced the diameter of nanofibers. The nanofiber diameter of the composite membranes was within 200 nm, and the distribution range of the nanofiber diameter was also narrow (Figures 3b–h; Table S2). It can also be seen from the SEM images that the obtained PLLA/IL

composite nanofiber membranes did not appear flocculent bifurcation or adhesion.

In order to investigate the effect of IL on the properties of spinning solution, electrospinning process, and fiber morphology, we have measured the conductivities of the PLLA spinning solution and the PLLA/IL spinning solutions. The results were shown in Figure S1. The conductivity of the PLLA spinning solution was 0.294 μS·cm⁻¹, while the conductivities

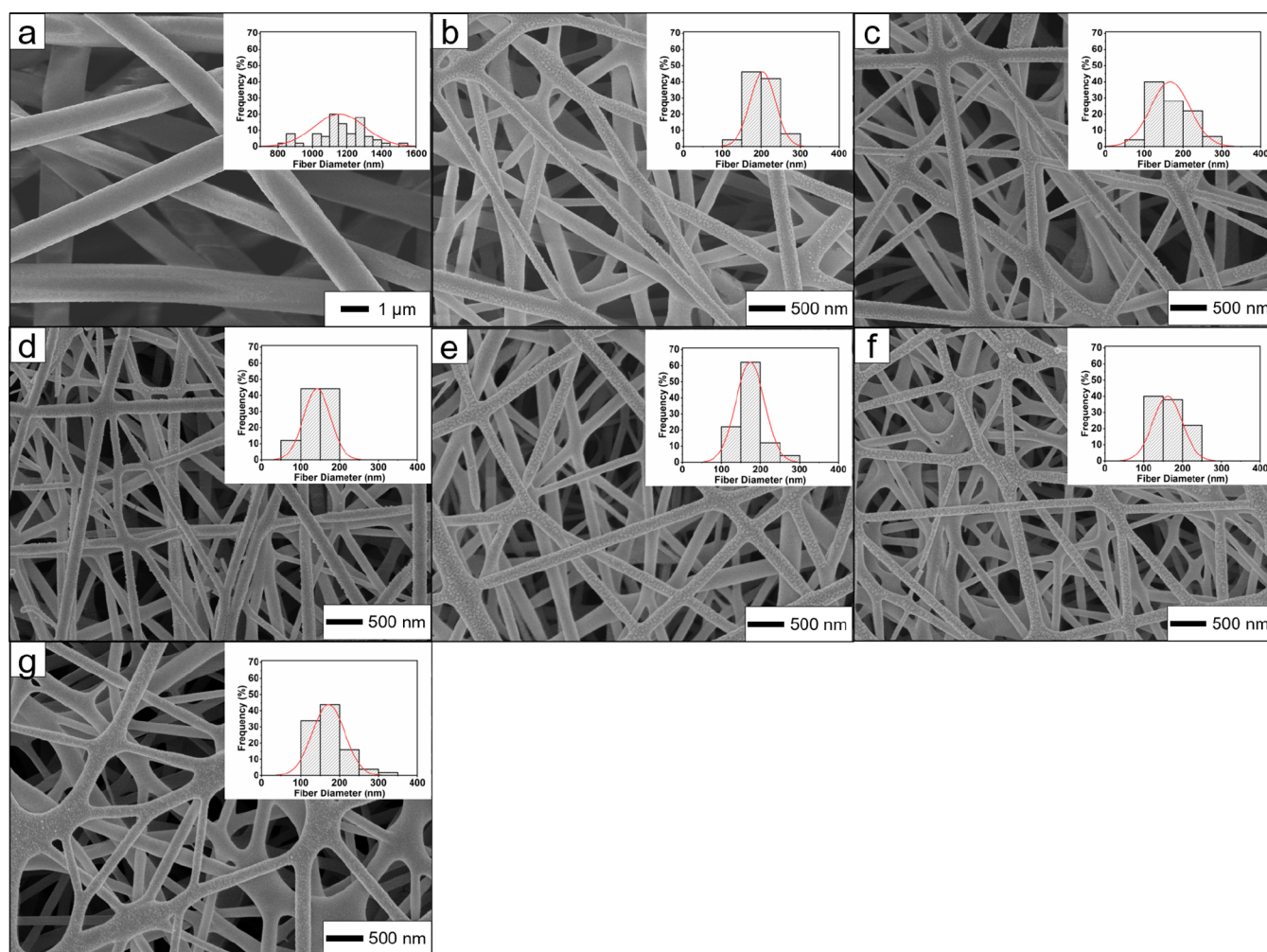


Figure 5. SEM images and fiber diameter distribution of nanofiber membranes: (a) PLLA; (b) PLLA-0.5%; (c) PLLA-1%; (d) PLLA-1.5%; (e) PLLA-2%; (f) PLLA-5%; (g) PLLA-8%.

of PLLA/IL spinning solutions increased by 2 orders of magnitude. The conductivities of different spinning solutions were compared with SEM images (Figures 2 and 3; Figure S1). It indicated that excessive conductivity of the spinning solution could cause flocculent bifurcation or adhesion of the nanofibers. For example, the conductivities of PLLA composite spinning solution with [EMIm][Cl], [EMIm][BF₄], and [EMIm][OAc] were 739 $\mu\text{S}\cdot\text{cm}^{-1}$, 444 $\mu\text{S}\cdot\text{cm}^{-1}$, and 673 $\mu\text{S}\cdot\text{cm}^{-1}$, respectively. The morphologies of nanofiber membranes prepared under the above three spinning solutions were poor (Figure 2b,c,f). Other spinning solutions, such as [EMIm][PF₆] with conductivity below 400 $\mu\text{S}\cdot\text{cm}^{-1}$, could successfully prepare nanofiber membranes with a narrow fiber diameter distribution. Therefore, the addition of IL could increase the conductivity of the spinning solution, thereby improving the morphology of the composite nanofiber membranes. However, the increase of conductivity needed to be kept within reasonable limits. When the conductivity exceeded 400 $\mu\text{S}\cdot\text{cm}^{-1}$, the tangential electric field along the surface of the droplet was offset by the droplets with too high conductivity, and Taylor cone could not be formed,³⁰ thus affecting the successful preparation of nanofiber membranes.

After investigating the effects of ILs on the morphology of PLLA nanofiber membranes, we tested the effects of ILs on the piezoelectric properties of PLLA nanofiber membranes. By

changing the types of IL anions and cations, a series of composite nanofiber membranes were spun by electrospinning, and the piezoelectric properties of PLLA/IL nanofiber membranes were tested at a pressure of 5 N. As seen from Figure 4, the piezoelectric properties of PLLA/IL composite nanofiber membranes were significantly different. The PLLA/[EMIm][BF₄] nanofiber membrane and the PLLA/[EMIm][PF₆] nanofiber membrane exhibited the best piezoelectric properties, and the voltage was about 3 times that of the PLLA nanofiber membrane. The results indicated that there was no significant correlation between the piezoelectric properties of the material and the specific microstructure of the ionic liquid. Moreover, the fiber morphology of the PLLA/[EMIm][BF₄] nanofiber membrane was poor (Figure 2c), which demonstrated that the piezoelectric properties were independent of the fiber morphology. The experimental data could also prove that the electrical conductivity was not related to the piezoelectric test results. As could be seen from Figure S1a, the spinning solution with the highest electrical conductivity was PLLA/[EMIm][Cl], but the piezoelectric properties of the nanofiber membrane prepared by it were poor (Figure 4a). In Figure S1a, the electrical conductivity of PLLA/[EMIm][BF₄] was at a medium value, but the output voltage of the fiber membrane was lower than that of the fiber membrane prepared by PLLA/[EMIm][PF₆] spinning solution with lower electrical

conductivity (Figure 4a). In Figure S1b and Figure 4b, the output voltages of the fiber membranes prepared by spinning solutions with similar electrical conductivities, such as PLLA/[BPY][PF₆], PLLA/[EMIm][PF₆], and PLLA/[EMIm][PF₆], differed greatly. In addition, the piezoelectric mechanism of PLLA was related to the orientation of the C=O dipole, so the fiber density was also independent of the piezoelectric properties. Therefore, [EMIm][PF₆], the IL that could improve both the PLLA nanofiber morphology and the piezoelectric properties, was selected for further study.

We studied the effects of different [EMIm][PF₆] additions on the morphology and properties of PLLA nanofiber membranes. The PLLA/[EMIm][PF₆] nanofiber membranes with different [EMIm][PF₆] contents were characterized by SEM (Figure 5). Compared to the PLLA nanofiber membrane (Figure 5a), the fiber diameters of PLLA/IL nanofiber membranes with different [EMIm][PF₆] contents were significantly reduced, and the distributions were narrow, mainly concentrated in 100–200 nm (Table S3). When the content of [EMIm][PF₆] exceeded 8 wt % of PLLA, the adhesion between the fibers became more obvious (Figure 5g). The above results showed that the addition of an IL could reduce the diameter of nanofibers, narrow the distribution range of fiber diameter, and effectively improve the morphology of composite nanofibers.

Comparing the conductivity of the PLLA/[EMIm][PF₆] spinning solution with different IL additions, the conductivity increased linearly with the increase of [EMIm][PF₆] addition (Figure S2). When the addition of [EMIm][PF₆] exceeded 8 wt % of PLLA, the conductivity was as high as 483 $\mu\text{S}\cdot\text{cm}^{-1}$, and the fibers were adhered at this time, which confirmed our conclusion in the previous part, that was, when the conductivity of the spinning solution exceeded 400 $\mu\text{S}\cdot\text{cm}^{-1}$, nanofiber membranes with excellent surface morphology could not be spun.

In order to investigate the effect of IL concentration on the piezoelectric properties, we have tested the piezoelectric properties of PLLA/[EMIm][PF₆] composite nanofiber membranes with different [EMIm][PF₆] contents (PLLA, PLLA-0.5%, PLLA-1%, PLLA-1.5%, PLLA-2%, PLLA-5%, and PLLA-8%). As shown in Figure 6, the piezoelectric perform-

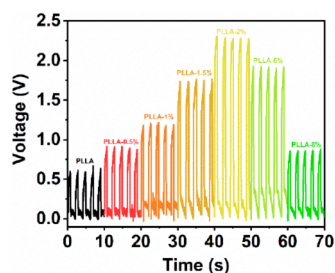


Figure 6. Piezoelectric test results of nanofiber membranes with different [EMIm][PF₆] contents.

ance of the PLLA nanofiber membrane was poor, and the output voltage was about 0.6 V. The piezoelectric properties of the PLLA/[EMIm][PF₆] nanofiber membranes were significantly improved. When the content of [EMIm][PF₆] was in the range of 0–2 wt %, the output voltage increased with the increase of the content of [EMIm][PF₆]. This was because in this range, the conductivity of PLLA/[EMIm][PF₆] spinning solution increased, so that under the action of high voltage in

the spinning process, the polarization of C=O in PLLA molecules was improved by increasing the conductivity of the spinning solution, thus promoting the directional arrangement of dipoles with the positive and negative charges to both sides of the molecular chain and showed a more ordered structure. In addition, due to the electronegativity of the O atom in C=O on the PLLA molecular chain, it could interact with the [EMIm]⁺ cation in [EMIm][PF₆], which increased the positive charge of the C atom in C=O.³¹ Therefore, the addition of [EMIm][PF₆] could increase the dipole moment of C=O, and the piezoelectric properties of the material would increase accordingly. However, when the addition of [EMIm][PF₆] continued to increase (2–8 wt %), the output voltage of the PLLA/[EMIm][PF₆] nanofiber membranes gradually decreased. The reason may be that with the increase of [EMIm][PF₆] addition, the amount of [EMIm]⁺ increased, resulting in the increase of steric hindrance, which inhibited the rotation of C=O dipoles in the microstructure, so the piezoelectric properties were weakened.³² Therefore, the optimal addition amount of [EMIm][PF₆] was 2 wt %, that is, PLLA-2% was the composite nanofiber membrane with the best piezoelectric properties. At this time, the dipole moment of C=O was large and could rotate relatively freely. Under the pressure of 5 N, the output voltage could reach 2.3 V, which was 4 times that of the PLLA nanofiber membrane. The above results showed that the concentration of IL could significantly affect the piezoelectric properties of nanofiber membranes.

XRD and DSC were used to explore the microstructure changes of PLLA after adding [EMIm][PF₆]. As could be seen from the XRD patterns (Figure S3), due to the fast fiber solidification rate during the electrospinning process, it was difficult to crystallize, and the PLLA and PLLA/[EMIm][PF₆] nanofiber membranes did not show obvious characteristic peaks.³³ Therefore, ionic liquid had no effect on the crystallization of the material, and the improvement of the piezoelectric properties of PLLA/[EMIm][PF₆] composite nanofiber membranes was independent of the crystallinity of the material. The DSC results showed that the glass transition temperature of PLLA/[EMIm][PF₆] nanofiber membranes was about 10 °C higher than that of PLLA during the heating process, which indicated that the PLLA and [EMIm][PF₆] were successfully compounded together (Figure S4a). During the cooling process (Figure S4b), PLLA membranes appeared a cold crystallization peak, while PLLA/[EMIm][PF₆] membranes did not, indicating that [EMIm][PF₆] combined with PLLA weakened the crystallization ability of the material, which was a benefit to the slight rotation of the dipole under the force, thus improving the piezoelectric properties of the composite.

Figure 7 is the FTIR spectra of composite nanofiber membranes with different [EMIm][PF₆] additions. The characteristic peak of PLLA at 1754 cm^{-1} was attributed to C=O on the PLLA ester group, and the characteristic peaks at 1183 and 1088 cm^{-1} were attributed to C–O–C. The PLLA nanofiber membrane and PLLA/IL composite nanofiber membranes had similar infrared spectra curves. This was because the concentration of [EMIm][PF₆] was too low, and the peak intensity of [EMIm][PF₆] was weak compared to the peak intensity of PLLA, so it was hardly shown in the figure. But we could still get useful information from Figure 7b, and the C=O stretching vibration peak attributed to PLLA shifted from 1754 to 1756 cm^{-1} , which confirmed that [EMIm][PF₆]

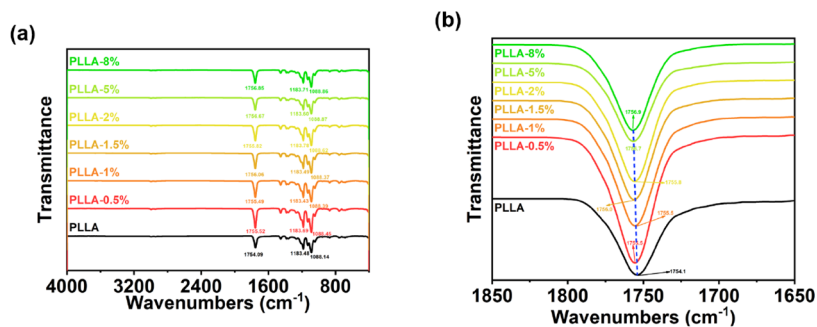


Figure 7. FTIR spectra of nanofiber membranes with different [EMIm][PF₆] additions: (a) General diagram; (b) 1650–1850 cm⁻¹ spectra.

existed in the PLLA/[EMIm][PF₆] composite nanofiber membrane and interacted with PLLA.

We also explored the influence of different pressures on the signal output value of the PLLA-2% composite nanofiber membrane (Figure 8). It showed that the output voltage

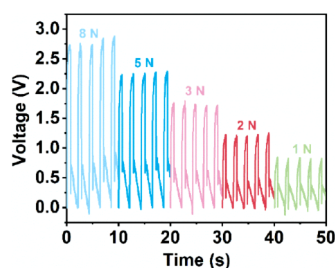


Figure 8. Piezoelectric test results of the PLLA-2% nanofiber membrane under different pressures.

increased with the increase of the tapping pressure. In order to test the stability of the composite nanofiber membrane, we used a linear motor as a device to exert constant pressure, and the results are shown in Figure S5. The piezoelectric performance did not decrease after a long period of use, indicating the good stability.

The effect of the IL on the degradation performance of PLLA was also investigated. The PLLA nanofiber membrane and PLLA-2% nanofiber membrane were placed in 0.1 mol·L⁻¹ NaOH solution. According to the results, the PLLA-2% nanofiber membrane showed a faster degradation rate within 5 h (Figure 9). It demonstrated that the addition of IL contributed to the degradation of PLLA. Hydrophobicity is an important characteristic of nanofiber membrane as a piezoelectric sensor.³⁴ Through the water contact angle tests of the nanofiber membranes (Figure S6), the hydrophobicity

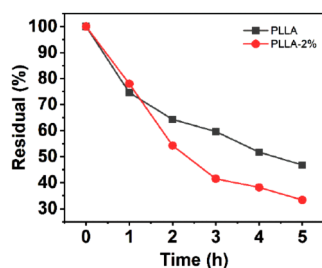


Figure 9. Degradation behavior of the PLLA nanofiber membrane and PLLA-2% nanofiber membrane in 0.1 mol·L⁻¹ NaOH solution.

of the composite nanofiber membrane did not change significantly after the addition of IL.

4. CONCLUSION

In summary, we have prepared a series of PLLA/IL composite nanofiber membranes to investigate the effects of ILs on the properties of spinning solution and the piezoelectric properties of PLLA. When the conductivity of the spinning solution was below 400 $\mu\text{S}\cdot\text{cm}^{-1}$, the addition of IL could improve the morphology and reduce the diameter of PLLA nanofibers significantly. According to the morphology and piezoelectric properties of the PLLA/IL composite nanofiber membranes, [EMIm][PF₆] was the best IL. When the addition amount of [EMIm][PF₆] was 2 wt %, the composite nanofiber membrane exhibited the best piezoelectric properties with the output voltage of 2.3 V under a pressure of 5 N, which was 4 times that of the PLLA nanofiber membrane. The improvement of the piezoelectric properties of PLLA/IL nanofiber membrane may be due to the high dipole moment generated by the C=O dipole after the interaction between the O atom in C=O on the PLLA molecular chain and the [EMIm]⁺ cation in the IL. In addition, the output voltage of composite nanofiber membrane increased with the increase of tapping pressure, and the PLLA/IL composite nanofiber membranes exhibited good stability, degradability, and hydrophobicity. The combination of IL and PLLA could effectively improve the morphology and piezoelectric properties of the material. More importantly, the strategy could provide a theoretical basis for the selection of the preparation system of piezoelectric polymer and inspire the development of environmentally friendly flexible piezoelectric materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at "https://pubs.acs.org/doi/10.1021/acsomega.3c08789?goto=supporting-info".

Conductivities of spinning solution with different kinds of ILs, conductivity of PLLA/IL spinning solution with different [EMIm][PF₆] contents, comparison of XRD patterns of PLLA and PLLA/[EMIm][PF₆] nanofiber membranes, comparison of DSC curves of PLLA and PLLA/[EMIm][PF₆] nanofiber membranes, stability test of PLLA-2% nanofiber membrane, water contact angle tests of nanofiber membranes with different [EMIm][PF₆] contents, the average thickness and fiber diameter of PLLA/IL ([EMIm]⁺ series) nanofiber membranes, the average thickness and fiber diameter of PLLA/IL ([PF₆]⁻ series) nanofiber membranes, and

the average thickness and fiber diameter of different [EMIm][PF₆] contents in PLLA/[EMIm][PF₆] nanofiber membranes (PDF)

AUTHOR INFORMATION

Corresponding Authors

Meng Cui – Beijing Key Laboratory of Clothing Materials R&D and Assessment, Beijing Engineering Research Center of Textile Nanofiber, School of Materials Science and Engineering, Beijing Institute of Fashion Technology, Beijing 100029, China; orcid.org/0000-0001-8909-125X; Email: cuiMeng@bift.edu.cn

Xiuqin Zhang – Beijing Key Laboratory of Clothing Materials R&D and Assessment, Beijing Engineering Research Center of Textile Nanofiber, School of Materials Science and Engineering, Beijing Institute of Fashion Technology, Beijing 100029, China; orcid.org/0000-0002-8687-4280; Email: clyzqx@bift.edu.cn

Authors

Xiaoxia Gu – Beijing Key Laboratory of Clothing Materials R&D and Assessment, Beijing Engineering Research Center of Textile Nanofiber, School of Materials Science and Engineering, Beijing Institute of Fashion Technology, Beijing 100029, China

Bin Wang – Beijing Key Laboratory of Clothing Materials R&D and Assessment, Beijing Engineering Research Center of Textile Nanofiber, School of Materials Science and Engineering, Beijing Institute of Fashion Technology, Beijing 100029, China; orcid.org/0000-0002-4957-9987

Guyue Liu – Beijing Key Laboratory of Clothing Materials R&D and Assessment, Beijing Engineering Research Center of Textile Nanofiber, School of Materials Science and Engineering, Beijing Institute of Fashion Technology, Beijing 100029, China

Jing Zhang – Beijing Key Laboratory of Clothing Materials R&D and Assessment, Beijing Engineering Research Center of Textile Nanofiber, School of Materials Science and Engineering, Beijing Institute of Fashion Technology, Beijing 100029, China; orcid.org/0000-0002-1516-3019

Rui Wang – Beijing Key Laboratory of Clothing Materials R&D and Assessment, Beijing Engineering Research Center of Textile Nanofiber, School of Materials Science and Engineering, Beijing Institute of Fashion Technology, Beijing 100029, China; orcid.org/0000-0001-5886-3261

Complete contact information is available at: <https://pubs.acs.org/10.1021/acsomega.3c08789>

Author Contributions

X.G., M.C., and X.Z. designed the research, conducted the experiments, and wrote the manuscript. B.W., G.L., J.Z., and R.W. participated in the discussion on the data.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (nos. 52173027, 52103069, and 51929301), the Young Elite Scientists Sponsorship Program by BAST (no. BYESS2023035), the Beijing Municipal Natural Science Foundation (no. 22JB0025), the Beijing Municipal

Commission of Education (no. KM202110012005), and the Beijing Scholars Program (no. RCQJ20303).

REFERENCES

- (1) Safaei, M.; Sodano, H. A.; Anton, S. R. A review of energy harvesting using piezoelectric materials: State-of-the-art a decade later (2008–2018). *Smart Mater. Struct.* **2019**, *28* (11), 113001.
- (2) Shivashankar, P.; Gopalakrishnan, S. Review on the use of piezoelectric materials for active vibration, noise, and flow control. *Smart Mater. Struct.* **2020**, *29* (5), 053001.
- (3) Huang, L.; Lin, S.; Xu, Z.; Zhou, H.; Duan, J.; Hu, B.; Zhou, J. Fiber-based energy conversion devices for human-body energy harvesting. *Adv. Mater.* **2020**, *32* (5), 1902034.
- (4) Liao, W.-Q.; Zhao, D.; Tang, Y.-Y.; Zhang, Y.; Li, P.-F.; Shi, P.-P.; Chen, X.-G.; You, Y.-M.; Xiong, R.-G. A molecular perovskite solid solution with piezoelectricity stronger than lead zirconate titanate. *Science* **2019**, *363* (6432), 1206–1210.
- (5) Berlincourt, D. Piezoelectric ceramics: Characteristics and applications. *J. Acoust. Soc. Am.* **1981**, *70* (6), 1586–1595.
- (6) Wu, J. Perovskite lead-free piezoelectric ceramics. *J. Appl. Phys.* **2020**, *127* (19), 190901.
- (7) Gao, J.; Xue, D.; Liu, W.; Zhou, C.; Ren, X. Recent progress on BaTiO₃-based piezoelectric ceramics for actuator applications. *Actuators* **2017**, *6* (3), 24.
- (8) Lu, L.; Ding, W.; Liu, J.; Yang, B. Flexible PVDF based piezoelectric nanogenerators. *Nano Energy* **2020**, *78*, 105251.
- (9) Ko, H.-U.; Kim, H. C.; Kim, J. W.; Park, J.; Kim, J. Soft piezoelectric polymer of poly[di(ethylene glycol) adipate] plasticized poly vinyl chloride and its strain sensing. *Mater. Lett.* **2018**, *227*, 276–280.
- (10) Zhao, G.; Zhang, X.; Cui, X.; Wang, S.; Liu, Z.; Deng, L.; Qi, A.; Qiao, X.; Li, L.; Pan, C.; Zhang, Y.; Li, L. Piezoelectric polyacrylonitrile nanofiber film-based dual-function self-powered flexible sensor. *ACS Appl. Mater. Interfaces* **2018**, *10* (18), 15855–15863.
- (11) Li, Q.-Q.; Wang, G.-K.; Liang, Z.-X.; Hu, Z.-J. Highly transparent and adhesive poly(vinylidene difluoride) films for self-powered piezoelectric touch sensors. *Chin. J. Polym. Sci.* **2022**, *40* (7), 726–737.
- (12) Habib, M.; Lantgios, I.; Hornbostel, K. A review of ceramic, polymer and composite piezoelectric materials. *J. Phys. D: Appl. Phys.* **2022**, *55* (42), 423002.
- (13) Stefaniak, K.; Masek, A. Green copolymers based on poly(lactic acid)-short review. *Materials* **2021**, *14* (18), 5254.
- (14) Du, X.; Zhao, C.; Zhang, J.; Ren, K. Study of field-induced chain conformation transformation in poly(l-lactic acid) based piezoelectric film by infrared spectroscopy. *J. Appl. Phys.* **2016**, *120* (16), 164101.
- (15) Lee, S. J.; Prabu, A. A.; Kim, K. J. Piezoelectric properties of electrospun poly(l-lactic acid) nanofiber web. *Mater. Lett.* **2015**, *148*, 58–62.
- (16) Choi, A. Y.; Sim, H. J.; Shin, M. K.; Kim, S. J.; Kim, Y. T. Residual charges during electrospinning assist in formation of piezoelectricity in poly(vinylidene fluoride-co-trifluoroethylene) nanofibers. *J. Nano Res.* **2015**, *37*, 13–19.
- (17) Li, B.; Hu, X.; Zhang, Q.; Peng, X.; Xiang, Y. Improved piezoelectricity of polylactide using vitamin B₂ for poling-free mechanical and acoustic nanogenerators. *J. Mater. Sci.* **2021**, *56* (1), 902–912.
- (18) Gu, X.; Cui, M.; Wang, B.; Zhang, C.; Zhu, Y.; Jin, X.; Wang, R.; Zhang, X. Electrospun environment-friendly poly(l-lactic acid)/CO₂-based polyurea nanofiber film for piezoelectric sensor. *Adv. Sustainable Syst.* **2023**, *7* (5), 2200441.
- (19) Martinis, E. M.; Berton, P.; Monasterio, R. P.; Wuilloud, R. G. Emerging ionic liquid-based techniques for total-metal and metal-speciation analysis. *TrAC, Trends Anal. Chem.* **2010**, *29* (10), 1184–1201.
- (20) Berthod, A.; Ruiz-Ángel, M. J.; Carda-Broch, S. Ionic liquids in separation techniques. *J. Chromatogr. A* **2008**, *1184* (1–2), 6–18.

- (21) Sun, P.; Armstrong, D. W. Ionic liquids in analytical chemistry. *Anal. Chim. Acta* **2010**, *661* (1), 1–16.
- (22) Ho, T. D.; Canestraro, A. J.; Anderson, J. L. Ionic liquids in solid-phase microextraction: A review. *Anal. Chim. Acta* **2011**, *695* (1–2), 18–43.
- (23) Dupont, J.; Consorti, C. S.; Spencer, J. Room temperature molten salts: Neoteric “green” solvents for chemical reactions and processes. *J. Braz. Chem. Soc.* **2000**, *11* (4), 337–344.
- (24) Liu, S.-J.; Zhou, F.; Zhao, L.; Xiao, X.-H.; Liu, X.; Jiang, S.-X. Immobilized 1,3-Dialkylimidazolium salts as new interface in HPLC separation. *Chem. Lett.* **2004**, *33* (5), 496–497.
- (25) Qiu, H.; Jiang, S.; Liu, X. N-methylimidazolium anion-exchange stationary phase for high-performance liquid chromatography. *J. Chromatogr. A* **2006**, *1103* (2), 265–270.
- (26) Na, B.; Zhang, P.; Lv, R.; Tian, R.; Ju, Y.; Liu, Q. Effect of ionic liquids on the morphology and mesophase formation of electrospun polylactide nanofibers. *Polymer* **2015**, *65*, 55–62.
- (27) Yarin, A. L.; Koombhongse, S.; Reneker, D. H. Taylor cone and jetting from liquid droplets in electrospinning of nanofibers. *J. Appl. Phys.* **2001**, *90* (9), 4836–4846.
- (28) Shi, Q.; He, S.; He, Y.; Wu, Y.; Liu, R. Enhanced the dielectric and piezoelectric properties of polyacrylonitrile piezoelectric composite fibers filled with ionic liquids. *J. Appl. Polym. Sci.* **2023**, *140* (19), No. e53824.
- (29) Varposhti, A. M.; Yousefzadeh, M.; Kowsari, E.; Latifi, M. Enhancement of β -phase crystalline structure and piezoelectric properties of flexible PVDF/ionic liquid surfactant composite nanofibers for potential application in sensing and self-powering. *Macromol. Mater. Eng.* **2020**, *305* (3), 1900796.
- (30) Angamma, C. J.; Member, S.; Jayaram, S. H. Analysis of the effects of solution conductivity on electrospinning process and fiber morphology. *IEEE Trans. Ind. Appl.* **2011**, *47* (3), 1109–1117.
- (31) Liu, H.; Zhao, R.; Song, X.; Liu, F.; Yu, S.; Liu, S.; Ge, X. Lewis acidic ionic liquid [Bmim]FeCl₄ as a high efficient catalyst for methanolysis of poly (lactic acid). *Catal. Lett.* **2017**, *147* (9), 2298–2305.
- (32) Fukada, E. Recent developments of polar piezoelectric polymers. *IEEE Trans. Dielectr. Electr. Insul.* **2006**, *13* (5), 1110–1119.
- (33) Zhou, H.; Green, T. B.; Joo, Y. L. The thermal effects on electrospinning of polylactic acid melts. *Polymer* **2006**, *47* (21), 7497–7505.
- (34) Qu, F.; Zhang, S.; Huang, C.; Guo, X.; Zhu, Y.; Thomas, T.; Guo, H.; Attfield, J. P.; Yang, M. Surface functionalized sensors for humidity-independent gas detection. *Angew. Chem., Int. Ed.* **2021**, *60* (12), 6561–6566.