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Ionic-liquid-induced ferroelectric polarization in poly(vinylidene fluoride) thin films

Feipeng Wang,^{1,a)} Alexander Lack,¹ Zilal Xie,² Peter Fröbing,¹ Andreas Taubert,² and Reimund Gerhard¹

¹Applied Condensed-Matter Physics, Institute of Physics and Astronomy, University of Potsdam, 14476 Potsdam, Germany

²Institute of Chemistry, University of Potsdam, 14476 Potsdam, Germany

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Thin films of ferroelectric β -phase poly(vinylidene fluoride) (PVDF) were spin-coated from a solution that contained small amounts of the ionic liquid (IL) 1-ethyl-3-methylimidazolium nitrate. A remanent polarization of 60 mC/m² and a quasi-static pyroelectric coefficient of 19 μ C/m²K at 30 °C were observed in the films. It is suggested that the IL promotes the formation of the β phase through dipolar interactions between PVDF chain-molecules and the IL. The dipolar interactions are identified as Coulomb attraction between hydrogen atoms in PVDF chains and anions in IL. The strong crystallinity increase is probably caused by the same dipolar interaction as well. © 2012 American Institute of Physics. [doi:10.1063/1.3683526]

All-organic electronic devices, such as light-emitting diodes, solar cells or field-effect transistors, require high-quality organic memory elements that are also compatible with conventional silicon-based electronics.¹ Ferroelectric polymers such as poly(vinylidene fluoride) (PVDF) and its copolymer with trifluoroethylene (TrFE) have attracted considerable attention because of their potential for non-volatile memories—a key technology in the mobile-device industry.^{2–5} One of the major advantages of PVDF and its copolymers is their solubility in organic solvents. Permanent dipoles formed by hydrogen and fluorine atoms in the VDF unit can rotate around the carbon backbone under an electric field that is high enough to induce a change of the polymer-chain conformation; for the semi-crystalline polymer, this results in bi-stability of the ferroelectric polarization.⁶

Spin coating from solution is a convenient way to produce thin polymer films. Previous studies indicated that highly polar solvents can induce the polar β or γ phases in PVDF films, but this seems only to happen in micrometer-scale films, and the fraction of the polar phase strongly depends on the solvent evaporation rate.⁷ High-quality thin films of β -phase PVDF are still difficult to prepare. Good ferro- and piezoelectric properties are usually not achieved, and pyroelectricity is only rarely discussed. There is, thus, a need to improve the preparation and stabilization of thin films from β - or γ -phase PVDF.

In this letter, we introduce thin ferroelectric β -PVDF films spin-coated from a solution containing the ionic liquid (IL) 1-ethyl-3-methylimidazolium nitrate, [EMIM][NO₃], and discuss the factors that control crystallization, micro-structure, ferro- and pyroelectric properties.

The melting point of [EMIM][NO₃] (IoLiTec GmbH, Germany, cf. Figure 1) is approximately 38 °C, and its purity is better than 98%. PVDF powder (Solvay® 1008, Mw = 244 kg/mol) was dissolved in a mixture of dimethylfor-

amide (DMF) and acetone (50:50 v/v) with or without 5 wt. % of [EMIM][NO₃] to yield solutions with a polymer concentration of 50 g/l. PVDF with a thickness of about 430 nm was spin-coated at 1500 rpm for 20 s on aluminum-coated (50 nm) glass substrates. After drying at 100 °C and 24 h of vacuum annealing at 135 °C, another layer of aluminum (50 nm) was deposited on top of the polymer films as second planar electrode.

The crystalline phases of the PVDF were identified at room temperature (RT) via Fourier-transform infra-red spectroscopy (FTIR, Bruker Alpha, cf. Figure 2). When the films had been spin-coated from a solution without [EMIM][NO₃], dried and annealed, only the α phase was present, as evidenced by its characteristic IR bands, in particular at 532, 615, 763, and 1212 cm⁻¹.⁸ With [EMIM][NO₃] in the solution, the β phase of PVDF dominates: curves b and c in Figure 2 show typical IR signatures of the β phase, with characteristic bands at 510, 839, and 1276 cm⁻¹. In addition, the films contain γ -phase PVDF, as indicated by the band at 1234 cm⁻¹.

Figure 3(a) represents a scanning-electron-microscopy (SEM) image of an α -PVDF film prepared without [EMIM][NO₃]. The film contains spherulitic crystalline regions with diameters above 10 μ m. With [EMIM][NO₃], much smaller regions of about 1–3 μ m in diameter are observed, cf. Figure 3(b). Samples grown with [EMIM][NO₃], but dried at RT (instead of 100 °C), are particulates with high porosity (cf. Figure 3(c)), which cause problems during electrical poling.

Measurements of ferroelectric properties were performed with a home-made Sawyer-Tower circuit. Hysteresis loops were obtained by integrating non-linear current-

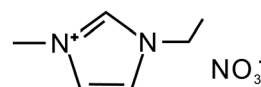


FIG. 1. Molecular structure of [EMIM][NO₃] ionic liquid.

^{a)} Author to whom correspondence should be addressed. Electronic mail: fpwang@canopus.physik.uni-potsdam.de.

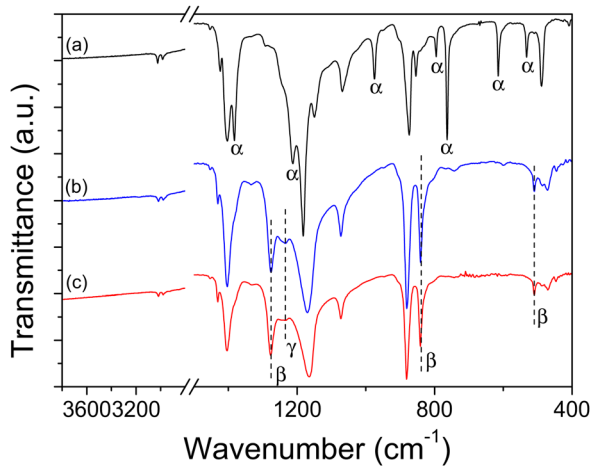


FIG. 2. (Color online) FTIR spectra of thin PVDF films (a) without and with, (b) 5 wt. %, and (c) 30 wt. % of [EMIM][NO₃].

voltage characteristics from a unipolar + bipolar electric-field sweep that allows separation of the ferroelectric switching from capacitive-charging and conduction processes.^{9,10} Figure 4 shows the ferroelectric hysteresis loop of β -phase PVDF films and the electric-field dependence of the sample current. The remanent polarization is approximately 60 mC/m², while the coercive field is around 200 MV/m. From conductivity measurements by means of dielectric spectroscopy, we know that the AC conductivities of our samples (at a frequency of 10 Hz) are around 10⁻¹³ S/m at RT and thus comparable to those of PVDF films without [EMIM][NO₃]. No ferroelectric hysteresis loop is observed on thin PVDF films without [EMIM][NO₃] added to the solution (α -PVDF).

For quasi-static pyroelectric-coefficient measurements, the dynamic short-circuit sample current in response to a slow sinusoidal temperature oscillation was determined in a Novocontrol Quatro system with a purpose-built sample holder.^{11,12} The experimental pyroelectric coefficient $p_{\text{exp}} = (1/A)(dQ/dT)$, defined as the temperature derivative of the charge density Q/A induced on the sample electrodes, was calculated from the measured total sample current as

$$p_{\text{exp}} = \frac{j_0 \sin \theta}{\omega T_0}, \quad (1)$$

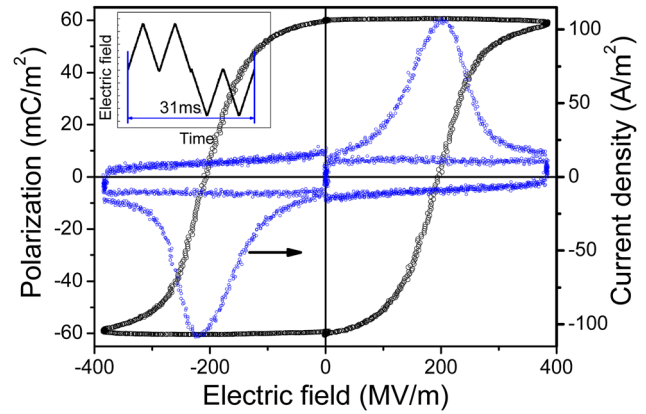


FIG. 4. (Color online) A typical ferroelectric hysteresis loop of thin PVDF films prepared with the addition of [EMIM][NO₃] to the solution. The blue curve represents the electric-field dependence of the measured current density. The inset shows the triangular bipolar + unipolar waveform used for the hysteresis measurements.

where ω and T_0 are the angular frequency and the amplitude of the sinusoidal temperature oscillation, respectively, and i_0 and θ are the amplitude of the current density and the phase shift between the oscillations of total current and temperature, respectively. The pyroelectric current is phase-shifted by $\theta = \pi/2$ with respect to the temperature, whereas non-pyroelectric currents due to relaxation and conduction are always in phase with the temperature. Therefore, the pyroelectric current can be separated into two parts by evaluating θ .

Figure 5(a) shows a typical current response from thin β -phase PVDF films at 30 °C. Numerical sinusoidal fitting allows the calculation of the temperature dependence of the pyroelectric coefficient p_{exp} between -20 and +60 °C, cf. Figure 5(b). At the low end of the investigated temperature range (-20 °C), p_{exp} is lower and θ is close to $\pi/2$ ($\theta = 0.42\pi$). At higher temperatures, θ decreases due to the increasing conductivity of the polymer films. p_{exp} increases to 18 $\mu\text{C}/(\text{m}^2\text{K})$ at 30 °C because of the decreasing elastic modulus of PVDF (thermal softening). Above 40 °C, the AC conductivity at a frequency of 10 Hz increases by nearly one decade (from 2.6×10^{-13} S/m at 20 °C to 2.3×10^{-12} S/m at 50 °C) which is mostly due to the melting of [EMIM][NO₃]. The enhanced conductivity causes a phase-shift (θ) decrease

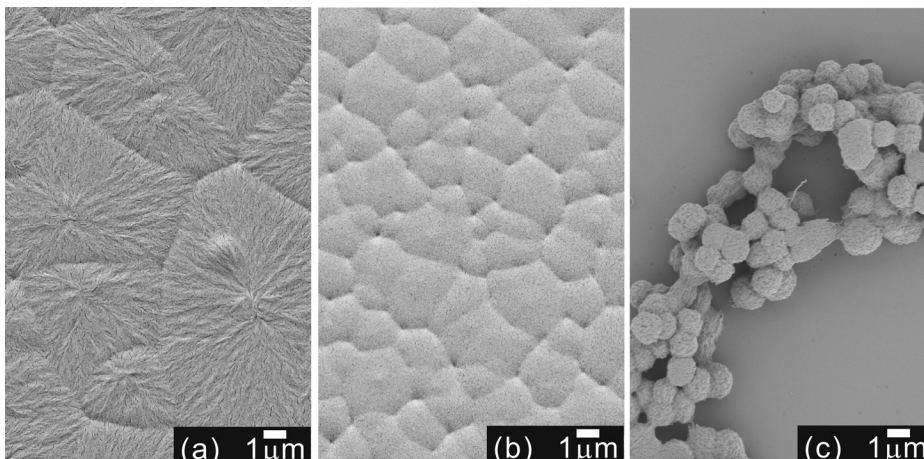


FIG. 3. Field-emission SEM photographs of the surfaces of thin PVDF films dried at 100 °C (a) without and, (b) with addition of [EMIM][NO₃] to the solution, as well as (c) dried at room temperature, with addition of [EMIM][NO₃] to the solution.

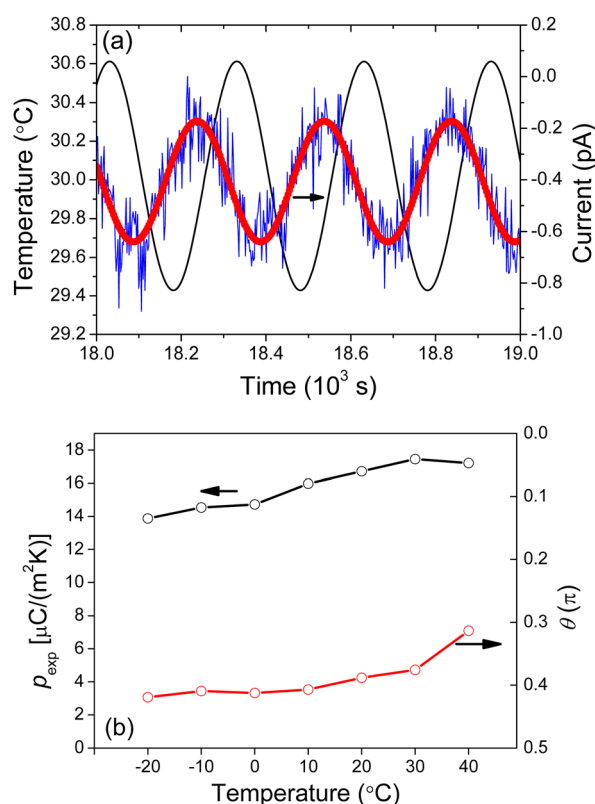


FIG. 5. (Color online) (a) Example of a quasi-static pyroelectrical measurement (period and amplitude of the sinusoidal temperature oscillation are 300 s and 0.6 K, respectively). The sinusoidal fitting of the short-circuit sample current is shown as bold curve (in red). (b) Temperature dependence of the quasi-static pyroelectric coefficient p_{exp} and of the phase shift θ of ferroelectric β -PVDF films.

between the total current and the temperature, which renders the determination of p_{exp} uncertain. Since the value of p_{exp} recovers to $18 \mu\text{C}/(\text{m}^2\text{K})$ after cooling to 30°C , this does, however, not indicate an irreversible decrease of the polarization.

Hydrogen bonding is visible in FTIR spectra from broad bands in the range of $3200\text{--}3500 \text{ cm}^{-1}$.¹³ However, in the current case, we do not observe any indication of hydrogen bonding, even at [EMIM][NO₃] concentration of 30 wt. %, Figure 2(c). Due to the absence of detectable hydrogen bonding, we assume that the ferroelectric β phase was mostly promoted by Coulomb interaction between the ionic liquid and molecular dipoles in the PVDF chains, *i.e.*, mainly by Coulomb attraction between protons in the CH₂ groups and anions in the ionic liquid.

Room-temperature ILs typically consist of bulky and asymmetric organic cations, and somewhat smaller anions. As the [EMIM]⁺ cation is fairly large, the NO₃[−] anion should favor the interaction with PVDF chains. Since each ion in an IL contains one unit of charge, the *extent-of-influence* of an ionic liquid generally depends on the size of the anion. In order to explore the tendency of the interaction between ionic liquid and PVDF, other [EMIM]⁺ ionic liquids, such as 1-ethyl-3-methylimidazolium trifluoromethane-sulfonate ([EMIM][CF₃SO₃]) and 1-ethyl-3-methylimidazolium ethylsulfate ([EMIM][C₂H₅SO₄]) were used to replace [EMIM][NO₃]. The melting points of [EMIM][CF₃SO₃] and [EMIM][C₂H₅SO₄] are -9 and -20°C ,^{14,15} respectively.

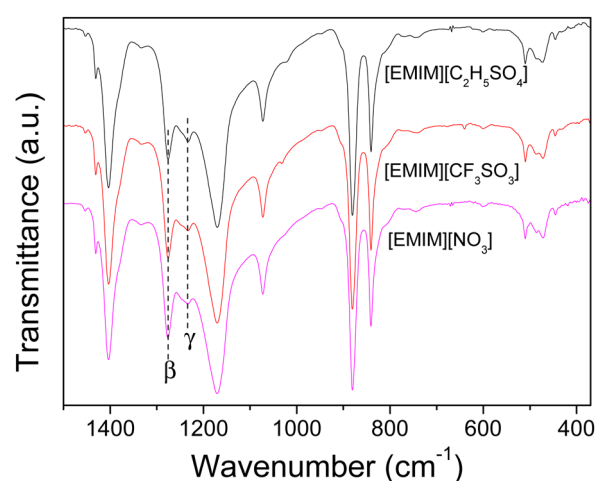


FIG. 6. (Color online) FTIR spectra of thin PVDF films prepared from solutions to which different ionic liquids (as indicated) had been added.

The molar percentage of the two ionic liquids in PVDF was adjusted to the same value as for [EMIM][NO₃]. All ionic liquids lead to β -phase-dominant PVDF films, as seen in the FTIR spectra of Figure 6. With increasing anion size, the β -phase content decreases and the γ -phase content increases (*cf.* the ratio of the IR bands at 1276 and 1234 cm^{-1} , see also Table I).

For the [EMIM]⁺ ionic liquids, the *extent-of-influence* decreases through the anion series of NO₃[−], CF₃SO₃[−], and C₂H₅SO₄[−]. The decrease correlates with increasing anion size and branching, hence a reduction in the interaction strength that is in this case determined by the distance between an anion and a CH₂ group of a PVDF chain. The interaction becomes weaker for larger anions, which results in a lower capability to induce polar phases in PVDF. This can explain why the β/γ ratio (proportional to the respective FTIR intensity ratio) decreases within the above series from [EMIM][NO₃] via [EMIM][CF₃SO₃] to [EMIM][C₂H₅SO₄] (*cf.* Table I).

During the crystallization of thin PVDF films, the rather high drying temperature of 100°C (much higher than the melting points of all three ionic liquids) keeps ions mobile. With the evaporation of the solvent, liquid-like clusters of PVDF molecules are formed, followed by rate-limited organization of the clusters into crystallite nuclei.¹⁶ The mobile ions lead to decreased cluster sizes which also tends to induce a larger number of nuclei. This could lead to smaller crystalline regions as observed in Figure 3(b). In addition, due to the dipolar interactions, dipoles within a nucleus are oriented perpendicular to the interface.¹⁷ Therefore, Coulomb forces from the anions would attract the hydrogen atoms in CH₂ groups of PVDF. The interaction forces PVDF chains into

TABLE I. Ratio of β to γ phase content in PVDF thin films.

Ionic liquid added in PVDF	Ratio of β/γ
[EMIM][NO ₃]	5.5
[EMIM][CF ₃ SO ₃]	4.3
[EMIM][C ₂ H ₅ SO ₄]	3.3

more extended chain conformations and better-oriented packing of $\text{CH}_2\text{-CF}_2$ dipoles, *i.e.*, into the all-*trans* conformation.

Coulomb attraction between the ionic liquid and the PVDF chains is expected to enhance the crystallinity of PVDF because of an increased number of nuclei and a better packing of molecular chains. From x-ray diffraction measurements (not shown here), we have noticed that the crystallinity of PVDF increased from 36% to 47% after the addition of 5 wt. % of [EMIM][NO_3] to the solution, which confirms our hypothesis.

Due to the extremely large number (approximately 10^{18}) of ionic-liquid molecules,¹⁸ it is not at all reasonable to conclude that only the Coulomb attraction between ionic-liquid molecules and PVDF molecular chains promotes the ferroelectric β phase of PVDF. However, as shown in this letter, the addition of some ionic-liquid molecules into a PVDF solution leads to thin β -phase PVDF films.

In conclusion, thin β -phase-dominant PVDF films were prepared by spin-coating a PVDF/(DMF + acetone) solution to which small amounts of an ionic liquid had been added. Sub-micrometer thin films were obtained after drying and annealing at elevated temperatures. Ionic liquids change the crystallization behavior of PVDF which is proven by much smaller crystalline regions in comparison with PVDF that had been prepared without the addition of [EMIM][NO_3] to the solution, and by the high occurrence of β -phase crystallites as well as the overall increase of crystallinity. The remanent polarization of the thin ferroelectric PVDF films can be as high as 60 mC/m², while the quasi-static pyroelectric coefficient reaches 18 $\mu\text{C}/(\text{m}^2\text{K})$ at 30 °C.

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