

Ionic liquids induce crystalline β phase and ferroelectric polarization in sub-micrometer films of poly(vinylidene fluoride) (PVDF)

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Abstract- In this paper, ferroelectric poly(vinylidene fluoride) (PVDF) films with a thickness of about 430 nm were obtained by spin coating from a solution that contained a small portion of the ionic liquid 1-ethyl-3-methylimidazolium nitrate ([EMIM][NO₃]). Before the experiments, the PVDF films were dried and thermally annealed. The sub-micrometer films on substrates show clear ferroelectric hysteresis behavior. A remanent polarization of about 60 mC/m² was detected by means of two independent methods: Non-linear current-voltage characteristics and time-dependent current response after application of voltage steps. The coercive field decreases from 190 to 165 MV/m when the width of triangular bipolar/unipolar electric-field cycles increases from 3 to 300 ms. Quasi-static pyroelectricity increases from 14 to 18 μ C/(m²K) between -20 and +40 °C. X-ray diffraction prove that the ionic liquid enhances the crystallinity. The dipolar interaction between anions of the ionic liquid and CH₂ groups in the PVDF chain during spin coating is considered to facilitate the formation of the β phase.

I. INTRODUCTION

Recent rapid developments in organic-based electronic devices require high-quality organic memory elements that should be compatible with conventional silicon-based devices, but which could eventually also lead to the implementation of all-organic electronics. Information-storage devices fabricated from ferroelectric polymers such as poly(vinylidene fluoride) (PVDF) and its copolymer with trifluoroethylene (TrFE) have attracted considerable attention because of their potential use in non-volatile memories — currently one of the most important technologies in the mobile-device industry. Permanent dipoles formed by hydrogen and fluorine atoms in the VDF unit can rotate around the carbon backbone in an electric field that is high enough to induce a change of the polymer-chain conformation, resulting in bi-stability.

Spin coating from solution is a convenient way to produce thin polymer films. Although some studies have indicated that highly polar solvents can induce the polar γ or β phases in PVDF films, this happens only in micrometer-scale films, and the polar-phase content is strongly influenced by the solvent evaporation rate [1]. Thin PVDF β -phase films of high quality are still difficult to prepare, and good ferro- and piezoelectric properties are usually not achieved, and pyroelectricity is only rarely mentioned or reported.

In this study, thin ferroelectric β -PVDF films have been spin-coated from a solution to which the ionic liquid 1-ethyl-3-methylimidazolium nitrate ([EMIM][NO₃]) had been added. Factors that influence crystallization and microstructure are discussed, since good ferro- and pyroelectric properties could be obtained on some of the thin spin-coated PVDF films.

II. EXPERIMENTAL DETAILS

A. Thin-Film Preparation

For preparing the solution, PVDF powder (Solvay® 1008, M_w=110,000 g/mol) was dissolved in a mixed solvent of dimethylformamide (DMF) and acetone (50:50 in volume) with or without the addition of 5 wt. % of [EMIM][NO₃]. The concentration was 50 g/l. The melting point of [EMIM][NO₃] is around 38 °C and its purity is better than 98% (IoLiTec GmbH, Germany). The molecular structure of [EMIM][NO₃] is shown in Fig. 1. Thin PVDF films with a thickness of about 430 nm were spin-coated at 1500 rpm for 20 s onto glass substrates with a 50 nm thick aluminum electrode in between. After drying at 100 °C and 24 h of vacuum annealing at 135 °C, another layer of aluminum (50 nm) was coated on top of the polymer films as second electric contact.

B. Structure Analysis and Electric Poling

The macromolecular conformation in the PVDF phases was probed at room temperature (RT) with a Fourier-Transform Infra-Red spectrometer (FTIR, Bruker Alpha) with a total of 32 scans and a wave-number resolution of 2 cm⁻¹. Wide angle X-ray Diffraction (XRD) (Siemens D5005) was employed to analyze the crystalline phases in the thin PVDF films.

The ferroelectric properties were characterized by means of a home-made Sawyer-Tower circuit. Hysteresis loops were obtained by integrating non-linear current-voltage curves from a unipolar/bipolar electric-field sweep that allows separation of ferroelectric switching from capacitive charging and conduction [2, 3]. The poling current is determined from the voltage across a reference resistance and is analyzed with

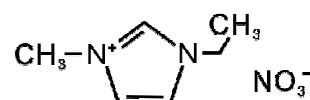


Figure 1. Molecular structure of the [EMIM][NO₃] ionic liquid.

respect to the different contributions from current-generating microscopic effects. The overall polarization P is calculated by integrating the polarization current over the poling time.

For poling under constant electric fields, the resulting currents through a thin PVDF film were monitored by means of an oscilloscope. The polarization was calculated according to the method described in Ref.[4].

For quasi-static pyroelectric-coefficient measurements, the dynamic short-circuit current of samples in response to an applied low-frequency sinusoidal temperature oscillation was determined in a Novocontrol Quattro system and a purpose-built sample holder [5, 6]. The experimental pyroelectric coefficient p_{exp} which is defined as the temperature derivative $p_{\text{exp}}=(1/A)(dQ/dT)$ of the charge density Q/A induced on the sample electrodes was calculated from the measured total current as

$$p_{\text{exp}} = (J_0 \sin \theta) / (\omega T_0), \quad (1)$$

where ω and T_0 are the angular frequency and the amplitude of the sinusoidal temperature oscillation, respectively. J_0 and θ are the amplitude of the current density and the phase shift between the oscillations of the total current and of the temperature. 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 easily separated from the overall current response by considering the phase shift θ .

III. RESULTS AND DISCUSSION

A. Crystallinity, Crystalline Phases and Chain Conformation

Fourier-transform infra-red (FTIR) spectra for the thin PVDF films prepared under different conditions are presented in Fig. 2. When the films were spin-coated from a solution without [EMIM][NO₃], dried and annealed, only the α phase was observable from its characteristic IR bands, in particular at 532, 615, 763, and 1212 cm⁻¹. With [EMIM][NO₃] added to the solution, the β phase dominated. Spectra (b) and (c) of Fig. 2 show typical IR results for the β phase, with characteristic bands at 510, 839 and 1276 cm⁻¹. In addition, the films contain a small amount of γ phase, indicated by the band

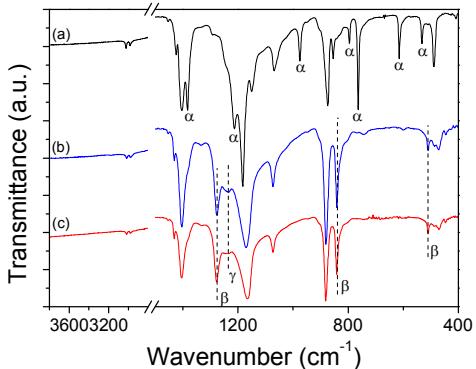


Figure 2. FTIR spectra of thin PVDF films without (a) and with (b) 5 wt. % and with (c) 30 wt. % of [EMIM][NO₃].

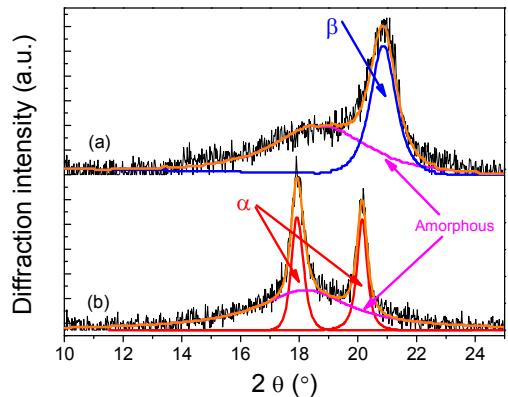


Figure 3. X ray diffractograms of samples with (a) or without (b) 5 wt% [EMIM][NO₃]. Crystalline phases are indicated according to peak fitting results.

at 1234 cm⁻¹.

Fig. 3 shows the XRD patterns for thin films with or without addition of 5 wt. % [EMIM][NO₃]. Thin PVDF films without [EMIM][NO₃] exhibit two peaks that correspond to the α phase (at 2 θ values of 17.9° and 20.14°). Addition of [EMIM][NO₃] results in the appearance of β -phase crystallites (at a 2 θ value of 20.5°), while the two peaks corresponding to α -phase crystallites disappear. In order to correlate the crystalline structure with the respective electrical behavior of the PVDF samples, the X-ray diffraction data of Fig. 3 were fitted with the Pearson VII function [7]. Crystallinity values are calculated from the area ratios of the crystalline peaks and the respective overall XRD patterns. It is found that the crystallinity of PVDF films is significantly enhanced to 47% from 36% after the addition of [EMIM][NO₃].

B. Ferroelectric Polarizaton and Pyroelectric Response

Fig. 4 shows the ferroelectric hysteresis loops for thin β -phase PVDF films. The remanent polarization reaches values up to about 60 mC/m², which is lower than the 70 mC/m² found on uniaxially stretched PVDF. The lower polarization is most probably due to the lower crystallinity, which is reasonable for spin-coated PVDF in comparison with stretched PVDF films. The coercive field decreases from 190 to 165 MV/m if the frequency of the applied electric field is lowered from 300 to 3 Hz. However, the remanent and the saturation polarization increase at lower frequency. The frequency dependencies of polarization and coercive field are caused by the interaction between space charge and dipoles in PVDF [8, 9]. At lower frequencies, there is sufficient time for space-charge motion to traps at the interface between the amorphous phase and the ordered polar phase. Here, trapped charge can stabilize the dipole orientation and thus causes higher remanent polarization [9]. The smaller values of the coercive field at lower frequencies probably originate from the longer time that is available for dipole orientation. Further investigation is required for better understanding the observed behavior. No ferroelectric hysteresis loop was found for thin PVDF films that had been prepared without [EMIM][NO₃].

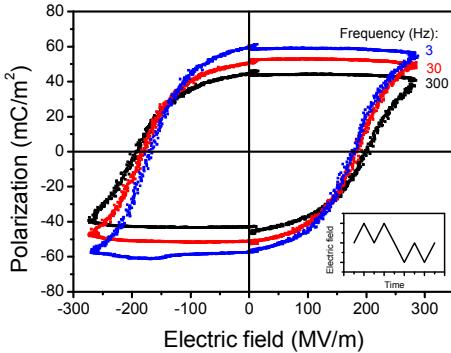


Figure 4. Typical ferroelectric hysteresis loops of thin PVDF films prepared with [EMIM][NO₃]. The inset shows one full cycle of the unipolar/bipolar voltage waveform employed for the measurements.

Poling thin PVDF films with [EMIM][NO₃] twice under the same electric field and the same polarity – but with a polarity opposite to the one previously used on the same sample – yields different poling currents as shown in Fig. 5. As expected, we observed a larger poling-current flow during the first switching experiment (curve a) than for the second poling (curve b). Because of the relatively short poling times, charge motion and trapping can be excluded as the main explanation for the poling behavior. It is concluded that a re-orientation of dipoles occurs during the first switching experiment. We calculate a polarization of approximately 58 mC/m² for poling with positive or negative electric fields of 300 MV/m.

The pyroelectric coefficient p_{exp} was measured between -20 and +60 °C at steps of 10 °C. Fig. 6(a) depicts a typical current response of thin β-phase PVDF films at 30 °C. After numerical sinusoidal fitting, the temperature dependence of the pyroelectric coefficient p_{exp} between -20 and +60 °C is calculated and shown in Fig. 6(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. p_{exp} increases with increasing temperature up to 18 μC/(m²K) at 30 °C because of the decreasing elastic modulus of PVDF. Above about 40 °C, the conductivity increases markedly, causing a decrease of the

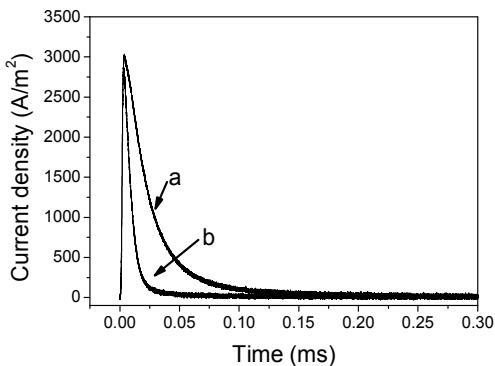


Figure 5. Time dependence of the poling current in thin PVDF films with [EMIM][NO₃] under a constant electric field of 300 MV/m. (a) poling with the opposite polarity compared to the previous poling (not shown), (b) second poling with the same polarity as in (a).

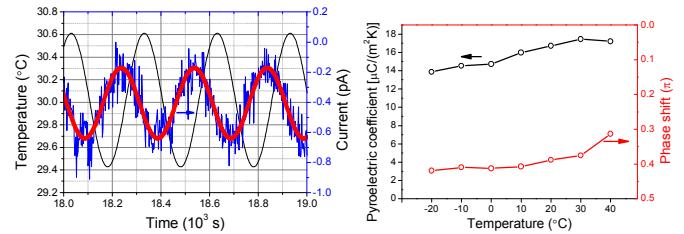


Figure 6. (a) Example of a quasi-static pyroelectric measurement (period and amplitude of the temperature oscillation 300 s and 0.6 K, respectively). The sinusoidal fitting for the short-current current response is shown in bold red. (b) Temperature dependence of the quasi-static pyroelectric coefficient p_{exp} of thin ferroelectric β-phase PVDF films.

phase shift θ between the total current and the temperature and thus rendering the determination of p_{exp} uncertain. This does, however, not indicate a lower polarization, but rather a larger polarization fluctuation at higher temperatures, since the value of p_{exp} recovers to 18 μC/(m²K) after cooling back to 30 °C.

C. β-Phase Formation in Thin PVDF Films after the Addition of [EMIM][NO₃] to the PVDF Solution

Hydrogen bonding is visible in FTIR spectra from broad bands in the range 3200–3500 cm⁻¹. However, there were no peaks detected in this region for any of the PVDF films prepared without or with [EMIM][NO₃], even when the [EMIM][NO₃] concentration reached 30 wt. %, as shown in Fig. 2(c). Due to the absence of hydrogen bonding, we assume that the ferroelectric β phase was promoted by Coulomb interaction between the ionic liquid and molecular dipoles in the PVDF chains, i.e. by Coulomb attraction between protons in the CH₂ groups and anions in the ionic liquid.

Room-temperature ionic liquids often consist of bulky and asymmetric organic cations and much smaller anions. Consequently, the polarity of an ionic liquid generally depends on the size of 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 trifluoromethanesulfonate ([EMIM][CF₃SO₃]) and 1-ethyl-3-methylimidazolium ethylsulfate ([EMIM][C₂H₅SO₄]) were employed instead of [EMIM][NO₃]. The melting points of [EMIM][CF₃SO₃] and [EMIM][C₂H₅SO₄] are -9 and -20 °C [10, 11], respectively. The molar percentage of the two ionic

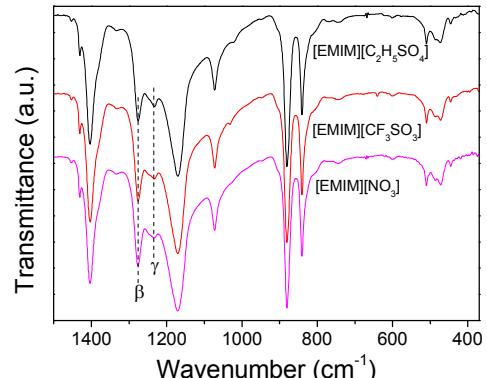


Figure 7. FTIR spectra of PVDF thin films with addition of different ionic liquids as marked in the legend.

liquids in PVDF was adjusted to the same value as with [EMIM][NO₃]. All ionic liquids lead to β -phase-dominant PVDF films, as seen in the FTIR spectra of Fig. 7. With increasing anion size, the β -phase content increases and the γ -phase content decreases (*cf.* the ratio of the IR bands at 1276 and at 1234 cm⁻¹).

For the [EMIM]⁺ ionic liquids, the polarity decreases through the anion series of NO₃⁻, CF₃SO₃⁻ and C₂H₅SO₄⁻. This decrease in polarity correlates with increasing anion size and with a reduction of the effective radius which is determined by the distance between the charge centroids of an anion and a CH₂ group in the 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 FTIR intensity ratio) decreases with the sequence from [EMIM][NO₃] via [EMIM][CF₃SO₃] to [EMIM][C₂H₅SO₄].

The dipolar interactions between the ionic liquid and the PVDF chains are expected to enhance the crystallinity of PVDF because of a better packing of the macromolecular chains. From X-ray diffraction measurements (see Fig. 3), we have noticed that the crystallinity of PVDF increased from 36% to 47% after the addition of 5 wt. % of [EMIM][NO₃] to the solution, which confirms our hypothesis.

IV. CONCLUSIONS

Thin β -phase-dominant PVDF films were prepared by spin-coating a PVDF/(DMF+acetone) solution to which ionic liquids had been added. Sub-micrometer films were obtained after drying and annealing at elevated temperatures. The occurrence of the β phase and the increase of crystallinity in PVDF after the addition of ionic liquids to the solution are assumed to be promoted by Coulomb interaction between anions and CH₂ groups in the PVDF macromolecules. 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 μ C/(m²K) at 30 °C.

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