Interrelation between Pyroelectricity and Residual Polarization in Thin Films of a Ferroelectric Polymer with Nanoscale Structure

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Polyvinylidene fluoride (PVDF), a typical ferroelectric polymer having a nanoscale structure, has prospects for widespread application in manufacturing pyroelectric sensors and transducers. In this paper, the relationship between pyroelectricity in PVDF thin films and the residual ferroelectric polarization is investigated on the basis of several experimental series. The pyroelectric coefficient is measured by the Collins dynamic method by analyzing the magnitude and shape of the voltage arising after irradiating a metal electrode with a light pulse. The residual polarization is measured by processing the plots of electrical signal resulting from application of high polarizing and switching voltage pulses to the sample. The wide ranges of pulse duration from 0.5 µs to 50 s, covering 8 orders of magnitude, and the applied electric field with a strength from 40 to 200 MV·m^{-1} are investigated. It has been found that the pyroelectric signal is directly proportional to the residual polarization and does not depend on the presence of the space charge. This result allows to obtain information on the state of polarization in PVDF by simply measuring its pyroelectric coefficient. The features of the pyroelectric behavior of PVDF films are analyzed and explained.

Keywords: Pyroelectricity, Nano-scale structure, Ferroelectric polymers, Polarization, Polyvinylidene fluoride, PVDF.

1. INTRODUCTION

During the last years, ferroelectric polymers having a nanocrystalline structure were considered as new candidates for replacing inorganic materials in pyroelectric sensors due to their good mechanical properties, reasonably sufficient performance and easy fabrication [1-5].

Polyvinylidene fluoride (PVDF) is a typical ferroelectric polymer. Its polymer chain has a structural formula of $–(CH_2\text{-}CF_2)n–$. The polarity of PVDF originates from the fact that CH_2 unit is an electron donor, while $CF2$ is an electron acceptor. Therefore, the dipole moment of the $(CH_2\text{-}CF_2)$ unit is rather high and equals to 2.3 D [6]. Polymer chains of PVDF are arranged in such a way that a semi-crystalline structure is formed consisting of nanosized crystallites and amorphous phase.

It has been established [7] that the crystalline component of PVDF has a lamellar structure. The average distance between adjacent lamellae is L_p = 13-14 nm, the crystalline lamella thickness is L_c = 6-7 nm, and the intercrystalline domain size is L_a = 7-8 nm [7]. The small-angle X-ray scattering (SAXS) revealed that crystalline and amorphous layers had fairly well defined sizes of about 10 nm each; and a diffuse-boundary of about 1.1 nm exists at the interface between the crystalline and amorphous phases [8]. The SAXS of PVDF exhibited a weak scattering peak at the magnitude of the scattering wave factor q = 0.55 nm^{-1}, corresponding to a crystal long period of 11.4 nm [9].

Out of three existing crystalline structures of PVDF, the so called β-phase crystals have the largest dipole moment and namely such films are used in infrared pyroelectric sensors [10].

Electro-physical phenomena leading to the appearance of the residual ferroelectric polarization in PVDF are the following. After initial formation of the β-phase nanocrystals, the macroscopic polarization of the film is equal to zero, because the dipole moments of particular β-phase nanocrystals are arranged chaotically. The preferential orientation of the dipoles occurs during application of a strong external DC electric field. The corresponding process of the macroscopic formation of the ferroelectric polarization is called "poling".

After poling and short-circuiting a thin film sample, it possesses the residual or remnant polarization P_r like any ferroelectric material. Presence of the residual polarization and its dependence on temperature T leads to the appearance of the pyroelectricity in PVDF.

Experimentally, the current $I(T) = dq/dt$ resulting from the temperature changes ($dT/dt \neq 0$) is usually measured, where q is the bound surface charge equal to the modulus of the P_r. The following expression is commonly used to define the pyroelectric coefficient

$$p = \frac{1}{S}\frac{dq}{dT} = \frac{1}{S}\frac{I(T)}{dT/dt}. \tag{1}$$

Fedosov and von Seggern studied pyroelectricity in PVDF [11] by a quasi-static method based on the analysis of the thermally stimulated depolarization (TSD) currents. The main difficulty of the quasi-static method consisted in separating the pyroelectric (reversible) component of the thermoelectric current from the relaxation (irreversible) component during the TSD measurements.

It was of interest to study the pyroelectric activity of PVDF experimentally also by a dynamic method, which is much simpler, in order to find interrelation between the pyroelectric coefficient p and the residual ferroelectric polarization P_r. This was intention of the

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present study where it has been proved that there is a direct proportionality between the residual polarization and the measured pyroelectric coefficient in PVDF in extremely wide ranges of poling and switching times and values of the externally applied electric field.

2. MATERIALS AND METHODS

Experiments were performed on 12.5 μm-thick bi-axially stretched PVDF samples from Kureha Co. with circular gold electrodes of $A = 0.64$ cm^2 area deposited by cathode sputtering. The structure of the polymer exhibited almost equal portion of crystalline and amorphous phases. IR spectra have shown that the fraction of the ferroelectric β-phase in relation to the non-polar α-phase corresponded to a ratio of 70:30 and this relation remained unchanged after poling.

Using the biaxial stretched PVDF films in this study ensured the presence of high residual polariza-tion, since it is precisely with such mechanical processing the non-polar α-phase is converted into the highly polar β-phase [10].

Initial poling and switching of polarization were performed by a step-wise application of high voltage in a setup described elsewhere [11, 12].

For modeling performance of a real infrared pyro-lectric sensor in view of thermal and electronic processes, the pyroelectric dynamic coefficient was measured by the thermal pulse method developed by Collins [13]. The idea of Collins's method is that a heat pulse is absorbed by the metal electrode deposited on the sample surface, so its temperature increases. The heat flows along the thickness direction creating a de-finite temperature distribution $T(x, t)$. The appearing pyroelectric displacement current is equal to the con-ductivity current in the measuring part of the circuit. It is assumed that the shape and value of the measured current are related to the value and distribution of po-larization and excess charges in the sample.

A light pulse of 50 μs duration was generated by the Metz 45 CT-3 flash unit and was used as a reproducible source of heat entering the surface of the electrified film. The pyroelectric signal was recorded using a Tek-tronix TDS 510A broadband oscilloscope (Fig. 1).
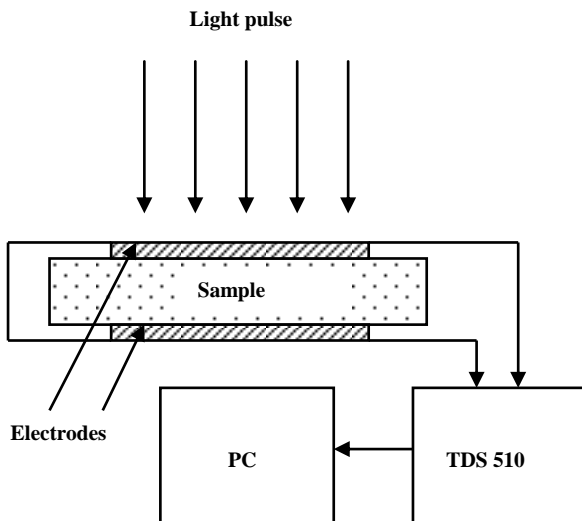

Fig. 1 – Schematic diagram of the experimental set-up

By using a highly sensitive pyroelectric detector, we have found that the light pulses were characterized by high reproducibility. The average energy spread in the measurement of successive 200 pulses was 2.4 %. The magnitude of the pyroelectric coefficient was judged by the maximum value of the electrical signal, so results were obtained not in absolute, but in relative units.

All measurements of pyroelectricity were performed at 26 °C. The samples were initially conditioned by poling in the field of 250 MV·m^{-1} during 50 s. We have previously found [14] that homogeneous and saturated polarization is formed under these conditions. After such poling, the polarization is easily switchable at any applied DC field, while the polarization distribution remains homogeneous [14]. The conditioning has been performed after each polarization reversal to guarantee the same initial conditions in all experiments.

Measurement of the ferroelectric polarization after application of the voltage pulses was performed by the method described in details elsewhere [11, 12].

3. RESULTS

Fig. 2 shows that the pyroelectric signal after initial poling of the sample at the highest applied voltage of 2.5 kV depends on duration of the poling pulse.
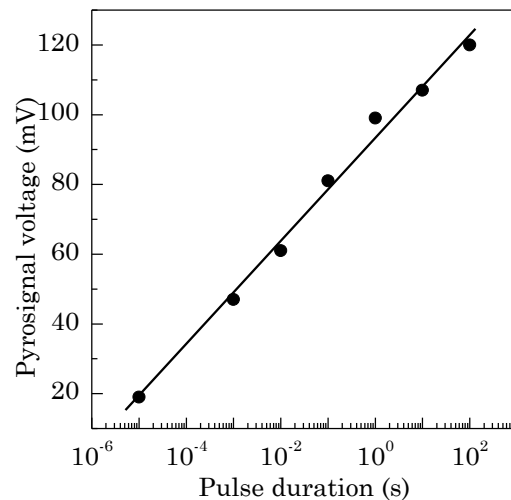

Fig. 2 – Dependence of the pyroelectric signal on the polariz-ing pulse duration in the range from 10 μs to 100 s during the primary electrification (poling) of the PVDF film with a vol-tage of 2.5 kV

As seen from Fig. 2, the highest value of the pyro-lectricity in our experiments was obtained only if the voltage pulse duration was equal to 100 s. As it has been shown in [14], the homogeneously distributed and easily switchable polarization is formed under this condition.

We performed five series of experiments, in which the polarization reversal was accomplished at different duration of the applied voltage pulses, but with the same voltage magnitude in each series. At a voltage of 0.5 kV that produced the field strength $E = 40$ MV·m^{-1}, i.e. of the same order as the coercive field of PVDF $E_c = 50$ MV·m^{-1} [11, 12], the pyroelectric signal de-creased only by 25.4 % even at the switching pulse du-ration of 50 s, while with the pulse duration less than

5 ms, there was practically no change of the pyroelectricity.

At 1 kV voltage applied for 50 s ($E = 80$ MV·m^{-1}), the pyroelectric signal decreased by 90.9 % indicating that the sample almost went to the state with zero average polarization. At this voltage, even for the pulse duration of 5 ms, 28.6 % of the pyroelectricity was lost. Increase in the pulse voltage to 1.5 kV ($E = 120$ MV·m^{-1}) led to the change in the sign of the pyroelectric voltage, if the voltage pulse duration was more than 50 ms. At the voltage pulse duration of 5 ms and at its value of 2 kV (160 MV·m^{-1}), the pyroelectric signal has already changed its sign. This indicated that the polarization vector inside the sample has changed its direction to the opposite one under the action of such a voltage pulse.

We have found that at the applied voltage of 2.5 kV (200 MV·m^{-1}) limited by a possibility of the electrical breakdown, the polarization has been completely switched from $+P_r$(max) to $-P_r$(max) due to application of only the 0.1 ms duration voltage pulse.

At the pulse duration of 100 s, the pyroelectric voltage had the same value as at the initial state of the sample, but it had the opposite sign. Thus, the initial polarization was completely reversed due to the application of such a pulse. It is interesting to note that our curves were very similar to A+ and A− curves in Fig. 6 of [15] corresponded to films heated by a laser beam. This proves the similarity of processes occurring during illumination of the sample by a laser beam and by a light pulse from the photo flash.

As follows from Fig. 3, the value of the pyroelectric signal after application of the same voltage depended not only on the total duration of the voltage pulses, but also on the number of the applied pulses. Namely, after application of five consecutive short voltage pulses of 10 μs duration each, the change of the pyroelectric signal was much smaller than after application of one 50 μs pulse in spite of the same total duration of the pulses in the two experiments. A probable reason of this feature is discussed in the next part of the paper.
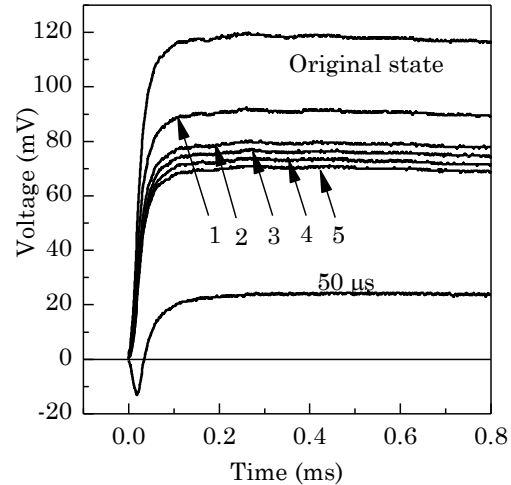
Finally, we compared evolutions of the pyroelectric voltage and the stable ferroelectric part of the polarization measured after consecutive application of the voltage pulses with increasing duration from 0.5 μs to 50 s at different field strength from 50 to 200 MV·m^{-1}, as shown in Fig. 4.

4. DISCUSSION

We consider a one-dimensional case taking into account that the linear dimensions of the sample, for example, its radius $r = 0.45$ cm is 360 times larger than the sample thickness $x_0 = 12.5$ μm. Thus, it is reasonable to assume that heat Q' absorbed by the metal electrode during its illumination by a light pulse diffuses only along the thickness direction of the sample x producing a specific temperature distribution.

By knowing the sample thickness x_o, we can find the diffusion time t_0 of the thermal wave passing through the sample from the following well-known equation:

$$x_0 \approx \sqrt{2\alpha \cdot t_0} \,, \qquad (2)$$

Fig. 3 – Pyroelectric signal after the sequential switching of polarization in PVDF films from a fully polarized state by applying 5 voltage pulses of 10 μs duration in comparison with the signal obtained after applying one voltage pulse of 50 μs duration: 1 – one voltage pulse, 2 – two voltage pulses, 3 – three voltage pulses, 4 – four voltage pulses, 5 – five voltage pulses. Voltage value of each pulse was 2.5 kV
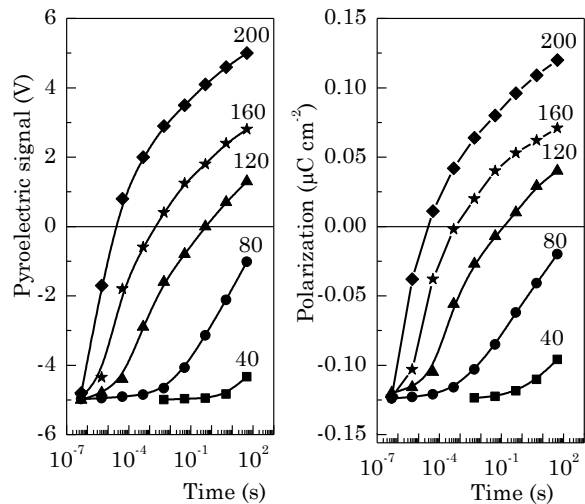
Fig. 4 – The evolution of the pyroelectric activity and the stable ferroelectric part of the polarization obtained by the series application of the voltage switching pulses with increasing duration from 0.5 μs to 50 s at different field strength. Magnitude of the field strength in MV·m^{-1} is shown near the corresponding curves

where α is the thermal diffusivity of PVDF

$$\alpha = \frac{k}{c \cdot p} \,, \qquad (3)$$

where $k = 0.17$ W·m^{-1}·K^{-1} is the thermal conductivity of PVDF, $c = 1380$ J·kg^{-1}·K^{-1} is the specific heat capacity, $\rho = 1800$ kg·m^{-3} is the specific gravity [16, 17]. Thus, $t_0 \approx 1$ ms and $a = 8·10^{-8}$ m^{2}s^{-1} from (2) and (3), therefore we limited the range of studied times by 0.8 ms (see Fig. 3).

Similarly to processes described during application of a laser beam to the ferroelectric polymer film [15], during the light pulse application, the heat Q' diffuses into the film producing a temperature distribution

$T(x, t)$ in the thickness direction x. The change of $T(x, t)$ with time t generates the displacement current in the sample. The current creates a voltage V_p between electrodes, which is measured using oscilloscope and PC (Fig. 1) and called the pyroelectric signal or voltage.

Table 1 – The proportionality coefficient γ (in nC cm^{-2} V^{-1}) between the values of the residual polarization P_r and the pyroelectric voltage V_p at different applied switching field strength and the duration of the switching voltage pulse applied to the completely polarized thin PVDF film

		Field strength (MV·m^{-1})				
		40	80	120	160	200
Duration of the pulse voltage	0.5 µs	30.8	30.8	30.8	30.8	30.8
	5 µs	32.3	30.5	28.3	32.5	28.0
	50 µs	30.0	32.3	32.5	28.5	30.0
	0.5 ms	28.3	28.3	32.3	28.5	30.3
	5 ms	30.0	29.3	29.3	28.0	29.5
	50 ms	–	31.5	29.0	27.3	30.0
	0.5 s	–	32.8	28.0	26.8	29.8
	5 s	–	28.0	27.5	28.5	30.0
	50 s	–	27.8	27.0	28.3	29.5

It is shown in Fig. 3 that the pyroelectric signal after the action of several consecutive short voltage pulses is much smaller than the pyroelectric signal measured after application of one pulse, the duration of which is equal to the total duration of several short pulses. This feature can be explained, if we assume that the switching time is not the same for all dipoles inside the sample, i. e. a part of the dipoles can be easily switched, while other dipoles require the longer time for switching. Then, only the "fast" dipoles will be switched under the action of the short voltage pulses. However, both "fast" and "slow" dipoles will be switched, if the voltage is applied for the longer time. In this case, the total switched polarization and consequently the value of the pyroelectric signal will be significantly increased. Namely this particular feature is observed in Fig. 3.

In order to establish the interrelation between the measured value of the pyroelectric signal and the residual polarization P_r, we analyzed data presented in Fig. 4 and have found the quotient from the division of the polarization by the pyroelectric signal for the same values of the applied field strength and the duration of the switching voltage application.

It is clear from the data of calculations presented in Table 1 that the interrelation between pyroelectricity and polarization in PVDF is characterized by the following figures: the mean value of the quotient (a peculiar coefficient of proportionality) is $\gamma \approx 29.5$ nC·cm^{-2}V^{-1} with the standard deviation of $\sigma = 6.7$ %. The deviation σ is not very large and obviously it is caused by uncontrolled random errors of experimental measurements and calculations.

Thus, the interrelation between the pyroelectric voltage V_p and the corresponding residual polarization P_r can be expressed as $V_p \approx \gamma P_r$. So, the pyroelectric signal in PVDF films is directly proportional to the residual polarization.

An important question arises: why the pyroelectricity depends only on the value of the residual polariza-

tion, but not affected by the presence of a space charge? Because it is known than along with the polarization, there may be a space charge in thin dielectric films subjected to electrical treatment. The main source of the space charge is injection currents from electrodes [16]. In order to clarify the effect of the space charge on the measured pyroelectricity we considered the Poisson equation, in accordance with which the excess space charge $\rho(x, t)$ can exist only in the regions, where the field strength and the polarization are inhomogeneous $(\partial P(x,t)/\partial x \neq 0)$ [14]

$$\varepsilon_o \varepsilon \frac{\partial E(x,t)}{\partial x} = \rho(x,t) - \frac{\partial P(x,t)}{\partial x}, \qquad (4)$$

where $\varepsilon_0 = 8.85 \cdot 10^{-12}$ F·m^{-1} is the vacuum permittivity, $\varepsilon \approx 20$ [11, 12, 14] is the dielectric constant of PVDF.

Due to the intrinsic conductivity, any free excess charges are neutralized in a short-circuited sample with the Maxwell relaxation time constant τ_M [15]

$$\tau_M = \frac{\varepsilon_0 \varepsilon}{g} \approx 6s, \qquad (5)$$

where $g = 3 \cdot 10^{-11}$ S·m^{-1} [12] is the electric conductivity of PVDF.

This indicates that any electric field will vanish in a short-circuited sample in a few seconds. Since the field becomes uniform $(E(x, t) = 0)$ after short-circuiting of the sample, then it follows from (9) that

$$\rho(x,t) = \frac{\partial P(x,t)}{\partial x}. \qquad (6)$$

If polarization is homogeneous $(P(x, t) = \text{const})$, as shown in [14], the charge $\rho(x, t) = 0$. Thus, the free space charge does not exist in the short-circuited PVDF and consequently it cannot affect the pyroelectricity. The screening charges deeply trapped at the boundaries of crystallites compensate the depolarizing field [12] and do not have any influence on the pyroelectricity.

5. CONCLUSIONS

In summary, we examined interrelation between the pyroelectricity in PVDF experimentally measured by the simple dynamic Collins method and the residual ferroelectric polarization. Original poling and polarization switching were performed by applying the high DC voltage pulses. Duration of the switching voltage pulses was in the range from 0.5 µs to 50 s, while the applied electric field strength was in the range from 40 to 200 MV·m^{-1}.

It has been found that the pyroelectric signal under all examined conditions is proportional to the residual ferroelectric polarization (Fig. 4 and Table 1). On the basis of the obtained results, we suggest to employ the measurement of the pyroelectricity by the Collins method for assessment of the polarized state in charged PVDF films, i.e. for estimating the magnitude and direction of the residual polarization. It is possible that this suggestion is applicable also for other ferroelectric polymers used for manufacturing of sensors and actuators.

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Взаємозв'язок між піроелектрикою та залишковою поляризацією в тонких плівках сегнетоелектричного полімеру з нанорозмірною структурою

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Полівініліденфторид (ПВДФ), який є типовим сегнетоелектричним полімером з нанорозмірною структурою, має перспективи широкого застосування для виготовлення піроелектричних датчиків і перетворювачів. У цій статті на основі декількох серій експериментів досліджено зв'язок між піроелектрикою в тонких плівках ПВДФ і залишковою сегнетоелектричною поляризацією. Піроелектричний коефіцієнт вимірювали динамічним методом Коллінза шляхом аналізу величини і форми напруги, що виникає після опромінення металевого електрода світловим імпульсом. Залишкову поляризацію вимірювали шляхом обробки графіків електричного зміщення, що виникає внаслідок впливу на зразок імпульсів високої поляризуючої і перемикаючої напруги. Досліджено широкі діапазони тривалості імпульсів від 0.5 мкс до 50 с, що охоплює 8 порядків величини, і прикладеного електричного поля з напруженістю від 40 до 200 МВ м$^{-1}$. Було встановлено, що піроелектричний сигнал прямо пропорційний величині залишкової поляризації і не залежить від наявності об'ємного заряду. Цей результат дозволяє отримати інформацію про стан поляризації в ПВДФ шляхом простого вимірювання його піроелектричного коефіцієнта. Проаналізовані і пояснені особливості піроелектричної поведінки плівок ПВДФ.

Ключові слова: Піроелектрика, Нанорозмірна структура, Сегнетоелектричні полімери, Поляризація, Полівініліденфторид (ПВДФ).