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Electroelastic effect in oriented polyvinylidene fluoride

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The influence of a DC electric field on mechanical properties of a film of oriented polyvinylidene fluoride (PVDF) was studied experimentally. The dynamic mechanical analysis and measurements of the spectrum of creep rates revealed changes in the elastic modulus, mechanical loss tangent, and creep rate upon application of an electric field with a strength of ~ 1 MV/m to the film. The elastic modulus increases irrespective of the field orientation relative to the direction of the film macroscopic polarization, which demonstrates the existence of a nonlinear electroelastic effect in PVDF.

Keywords: polyvinylidene fluoride, constant electric field, elastic modulus, electroelastic effect.

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Polyvinylidene fluoride (PVDF) is a piezoelectric polymer with a wide spectrum of practical applications in various devices [1], such as sensors [2], nanogenerators [3], supercapacitors [4], and microelectromechanical systems [5]. PVDF has a semicrystalline architecture and may form crystalline phases with nonzero spontaneous polarization that changes direction under the influence of a strong electric field. Therefore, PVDF belongs to the class of ferroelectric materials, but its physical and mechanical properties differ significantly from those of classical ferroelectric crystals. Specifically, PVDF is characterized by a very strong coercive field $E_c \sim 100$ MV/m [6] and a distinct polarization switching mechanism [7]. Since the amorphous phase of PVDF transitions to a highly elastic state at a temperature of about $-40\,^\circ$C [8], another important feature of this material is the capacity to undergo large reversible deformations at room temperature. This property makes it possible to produce flexible electronic devices based on PVDF films [3,9].

When used as an electromechanical transducer, PVDF is simultaneously subjected to an electric field and mechanical stresses. Therefore, it is of considerable interest to study the influence of electric fields on the mechanical properties of PVDF. In the present study, we examined experimentally the changes in longitudinal elastic modulus, mechanical loss tangent, and creep rate that arise upon application of a DC electric field (EF) to a film of oriented PVDF. These measurements are the first to reveal a nonlinear electroelastic effect, which manifests itself as an increase in elastic modulus at both parallel and antiparallel orientations of the field relative to the macroscopic film polarization.

A film of YD-1 PVDF (Shanghai Ofluorine Co., Ltd, PRC), which was produced by orientational stretching by 100 % at a temperature of $+120\,^\circ$C with subsequent poling in a strong EF applied via aluminum electrodes deposited on the film, was studied. This standard procedure [8] establishes a preferred orientation of polymer chains and residual macroscopic polarization orthogonal to the film surfaces. The measured density $\rho = 1.75$ g/cm^3 of the 100 μm-thick film and its piezoelectric coefficient $d_{31} \approx 14$ pC/N, which was determined by measuring the electric response of the film along the normal to the electrodes to a mechanical stress applied along the orientation axis, agree with literature data [8]. To determine the crystallinity of the studied material, which exerts a strong influence on the electromechanical properties of PVDF [8], we measured temperature dependences of the heat flow through the sample using differential scanning calorimetry (DSC) (Fig. 1, *a*). Degree of crystallinity K_{crys} of a semicrystalline polymer may be estimated as $K_{crys} = (\Delta H_m/\Delta H_m^0) \cdot 100\,\%$, where ΔH_m^0 and ΔH_m denote the enthalpy of fusion at 100 % crystallization of the polymer and its measured value, respectively [10]. Substituting $\Delta H_m^0 = 105$ J/g [11] and $\Delta H_m \approx 60$ J/g (Fig. 1, *a*) into this formula, we obtain $K_{crys} \approx 57\,\%$ for the studied PVDF film, which indicates that its amorphous phase content is close to 43 %.

A dynamic mechanical analysis (DMA) device produced by Seiko Instruments was used to study the influence of EF on the elastic modulus and mechanical loss tangent of the PVDF film. The DMS6100 measuring module of this device was fitted with a high-voltage chamber of a special design with electrodes that are fully isolated electrically from the module. The gap between these plane-parallel electrodes in the chamber was 1 mm, and they were significantly larger than the section of the film covered by aluminum electrodes deposited in vacuum (Fig. 2). The jaws of the DMA module enabled the application of variable force F to the film, which oscillated with a frequency of 1 Hz and induced longitudinal deformations with an amplitude lower than 0.1 %. The DMA device determined the elastic modulus and mechanical loss tangent six times per minute.

Since the mechanical characteristics of PVDF depend strongly on temperature (Fig. 1, *b*), measurements of the EF influence were performed at fixed temperature T. A certain

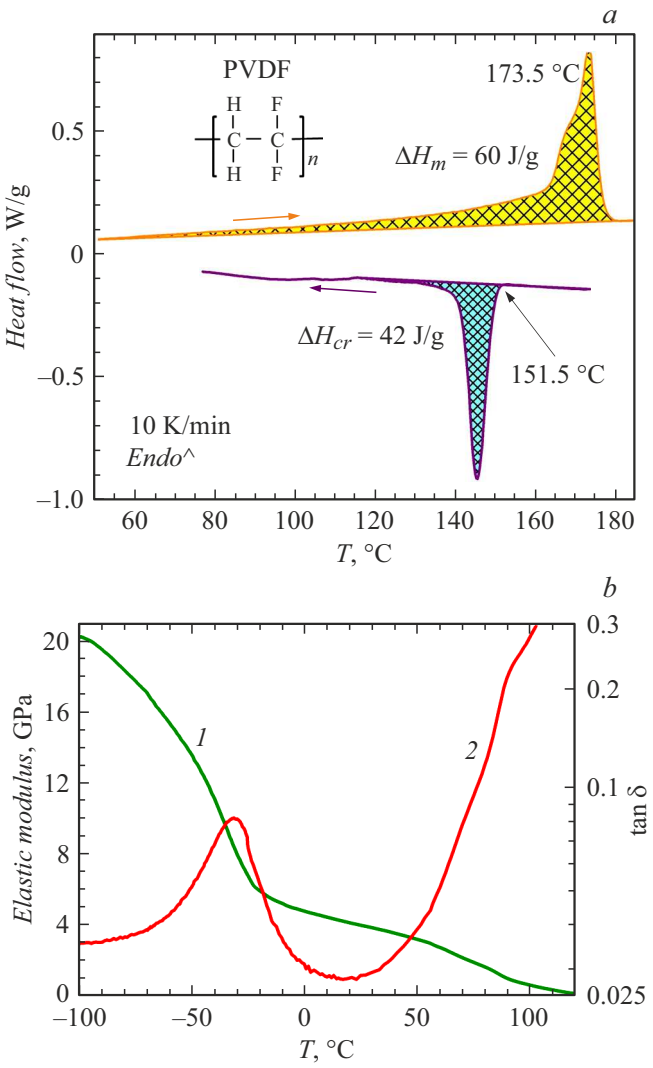

Figure 1. *a* — DSC curves obtained during the first scanning of PVDF. ΔH_m and ΔH_{cr} denote the enthalpies of melting and crystallization, respectively. *b* — Dependences of elastic modulus (*1*) and mechanical loss tangent $\tan\delta$ (*2*) on temperature T obtained by DMA.

DC voltage U ranging in amplitude from 5 to 8 kV was applied periodically between the external electrodes. The sample was kept under EF for 3–6 min, after which the electrodes were short-circuited for a similar period of time. This cycle was repeated several times, which allowed us to determine the mechanical parameters of the film with EF switched on and off and the form of their temporal variation.

A typical temporal dependence of the elastic modulus under voltage cycling is shown in Fig. 3, *a*. At zero EF, the modulus undergoes a gradual weak growth, which is caused by the elongation of polymer chains induced by the constant component of applied force F. The first application of EF leads to a step-like increase in elastic modulus. However, this change rapidly fades away, and the modulus reverts approximately to its preceding value. The observed reduction is probably caused by the flow of electric current across the film, which produces defective regions that lower the elastic modulus. With further voltage cycling, the modulus always increases in a step-like manner when EF is switched on and decreases sharply when EF is turned off (Fig. 3, *a*). The elastic modulus increases irrespective of the EF orientation relative to the direction of macroscopic film polarization (Fig. 3, *c*). This is an important feature of the discovered phenomenon, which may be termed the „electroelastic“ effect.

A similar experiment performed for tetrafluoroethylene (PTFE), which has a monomer unit with zero total dipole moment, revealed that its elastic modulus does not change after the application of EF. This result confirms that the observed effect is not associated with heating of PVDF in EF, which would reduce its elastic modulus. Furthermore, the lack of changes found in PTFE makes it possible to associate the electroelastic effect with the influence of EF on reorientations of polar monomer units of PVDF that should accompany longitudinal deformations of polymer chains arising in the process of mechanical measurements.

It should be noted that the electroelastic effect also manifests itself in step-like changes of the PVDF mechanical loss tangent, which arise when EF is switched on and off (Fig. 3, *b*), and is observed within the entire studied temperature range from −100 to 23 °C. Besides, tests of the PVDF film in the creep regime [12] revealed that

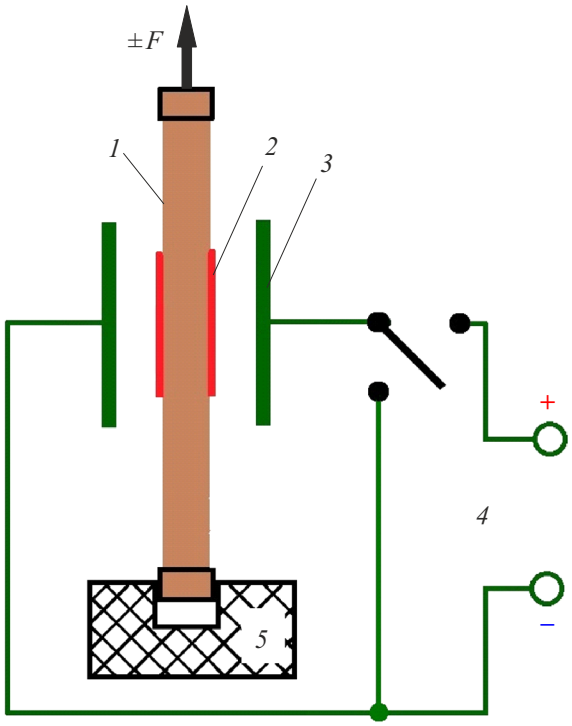

Figure 2. Diagram of the electromechanical experiment. *1* — Longitudinal cross-section of the PVDF film with a thickness of 0.1 mm, a length of 30 mm, and a width of 6 mm; *2* — aluminum electrodes 10 × 6 mm in size deposited on the film surfaces; *3* — external electrodes 16 × 9 mm in size producing EF in the sample; *4* — high DC voltage source; and *5* — immobile sample jaw.

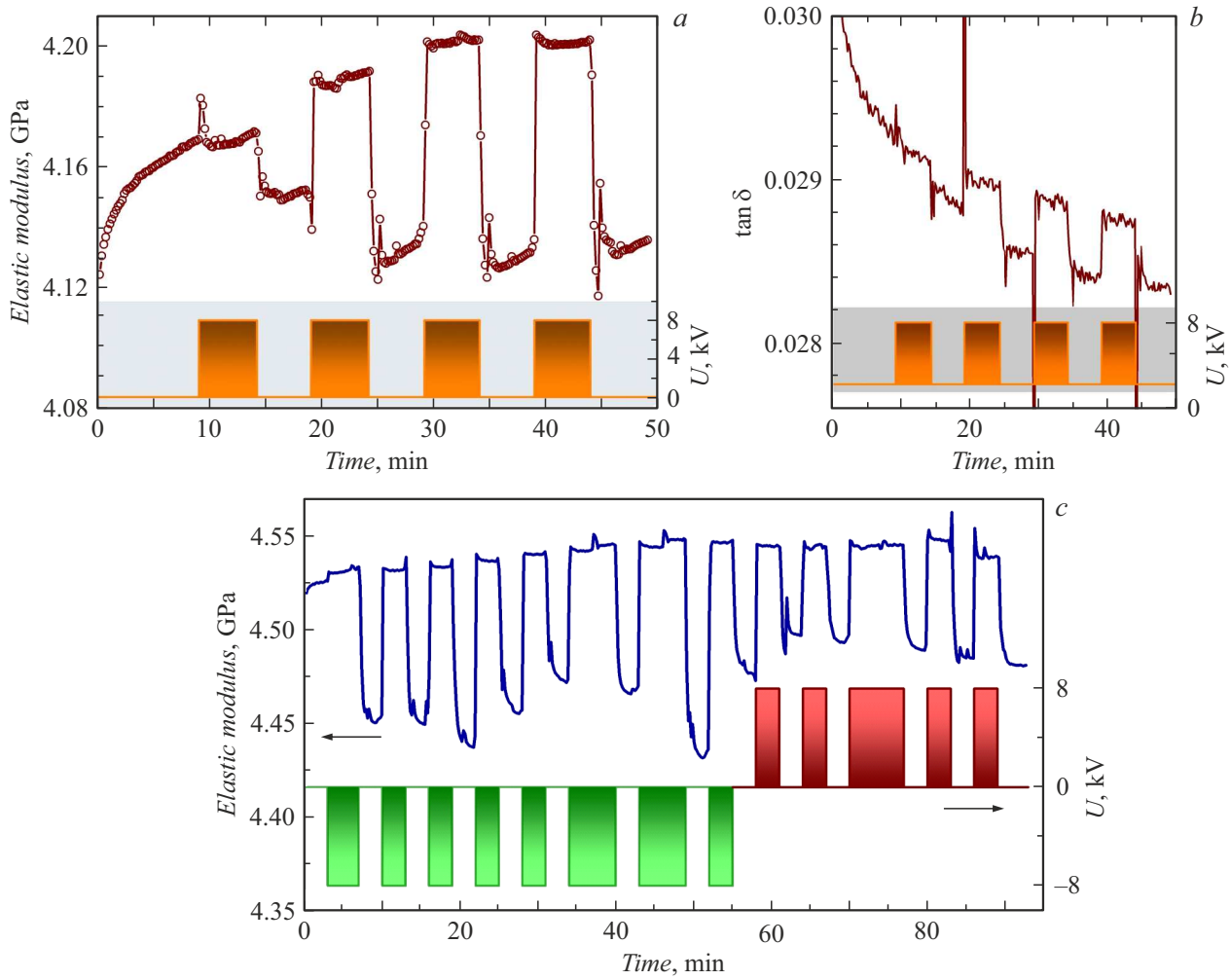

Figure 3. Temporal dependences of (a, c) elastic modulus and (b) mechanical loss tangent $\tan\delta$ of PVDF during cyclic application of a DC electric field to the film ($T = 23\,^{\circ}\mathrm{C}$, $U = 8\,\mathrm{kV}$).

deformation rate du/dt at constant mechanical stress σ increases for a short time after the application of EF (Fig. 4). This observation indicates that EF also affects the development of high elastic deformations in PVDF.

The magnitude of the electroelastic effect may be characterized by sensitivity η of longitudinal elastic modulus Y to EF, which is written as $\eta = \delta Y/(Y_0 E)$, where $Y_0 = Y(E = 0)$, $\delta Y = Y(E) - Y_0$, and E is the strength of EF within the PVDF film. Substituting thickness $d_f = 0.1\,\mathrm{mm}$ of the studied film, its relative permittivity $\varepsilon_f \approx 12$ [7], and distance $d \approx 1\,\mathrm{mm}$ between the external electrodes into formula $E = U/[d_f + \varepsilon_f(d - d_f)]$, we obtain EF strength $E \approx 0.7\,\mathrm{MV/m}$ at $U = 8\,\mathrm{kV}$. Therefore, variation $\delta Y/Y_0 \approx 1.5\,\%$ of the elastic modulus observed at $T = 23\,^{\circ}\mathrm{C}$ (Fig. 3, a) corresponds to electric sensitivity $\eta \approx 2 \cdot 10^{-8}\,\mathrm{m/V}$.

Since the elastic modulus increases at both positive and negative values of electric voltage U, the observed electroelastic effect is nonlinear. In the first approximation, it may be described by formula $Y(E) = Y_0 + AE + (1/2)BE^2$, where $A = \partial Y/\partial E$ and $B = \partial^2 Y/\partial E^2$ with the derivatives of modulus Y taken at $E = 0$. The linear term in the proposed relation explains the small change in $\delta Y(E)$ observed when the EF direction is reversed. Since the quadratic term produces the main contribution to $\delta Y(E)$, the revealed phenomenon differs significantly from the linear elastoelectric effect in ferroelectric crystals, which is due to the dependence of their elastic stiffnesses on the EF strength [13]. Apparently, the nonlinear electroelastic effect in PVDF is largely attributable to the influence of EF on reorientations of polar monomers $CH_2{-}CF_2$ that accompany mechanically induced deformations of polymer chains in the amorphous phase.

It should be noted that piezoelectric properties of the crystalline phase of PVDF also induce a dependence of the measured elastic modulus Y on EF. The influence of the piezoelectric effect may be estimated using equation of state $\sigma_1 = Yu_1 - e_{31}E_3$, where σ_1 is the mechanical stress inducing longitudinal deformation u_1 and $e_{31} = -\partial\sigma_1/\partial E_3 \approx 20\,\mu\mathrm{C/m^2}$ [14] is the piezoelectric

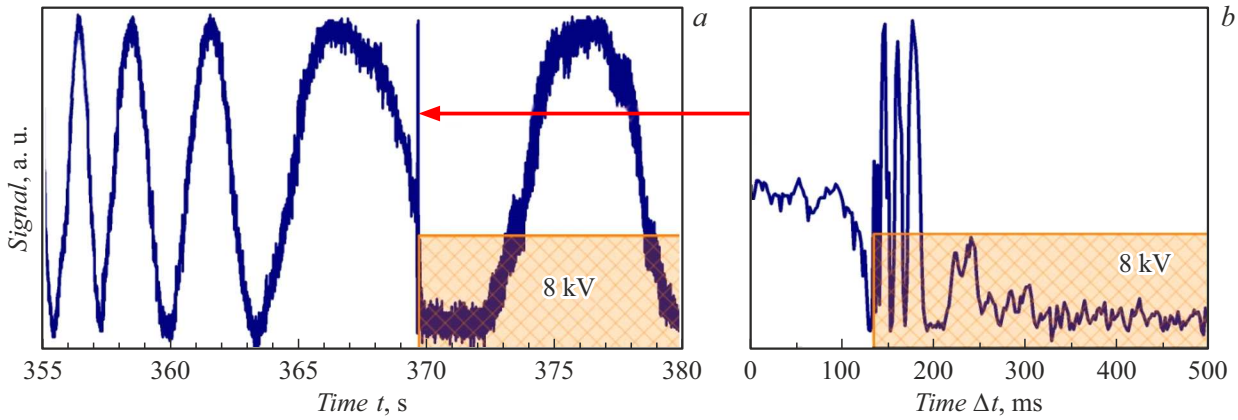

Figure 4. *a* — Interferometric signal characterizing the creep of a PVDF film ($\sigma = 120$ MPa, $T = +23\,^{\circ}$C) subjected to a DC EF ($U = 8$ kV). *b* — Signal variation after EF application, which reveals a short-term increase in deformation rate.

coefficient of PVDF that characterizes the σ_1 change under the influence of transverse electric field E_3. Since $Y \approx 4$ GPa and $u_1 \approx 0.1\,\%$ in the performed experiments, product $e_{31}E_3$ at $E_3 \approx 1$ MV/m turns out to be five orders of magnitude smaller than Yu_1. Therefore, the contribution of the piezoelectric effect is negligible in comparison with the measured changes $\delta Y > 40$ MPa (Fig. 3, *a*). EF-induced film deformation $\delta u_1 = e_{31}E_3/Y$ is also several orders of magnitude smaller than deformation jump $\delta u_1 \approx 0.03\,\%$ observed in the creep process after the application of EF (Fig. 4).

Thus, the nonlinear electroelastic effect in oriented PVDF was discovered and analyzed. The results of this study are important for predicting the behavior of this piezoelectric polymer under the influence of mechanical stresses and an electric field.

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Conflict of interest

The authors declare that they have no conflict of interest.

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