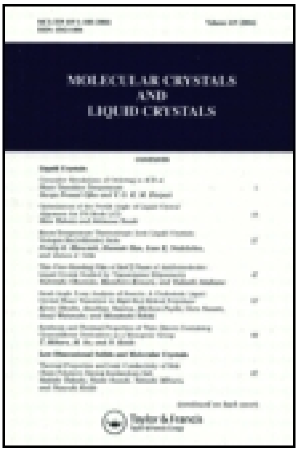

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Ferroelectric Switching of Thin Langmuir-Blodgett Films of P(VDF-TrFE) Copolymer: Comparison with Liquid Crystal Switching

L. M. Blinov [a], V. V. Lazarev [a], S. P. Palto [a] & S. G. Yudin [a]

[a] Shubnikov Institute of Crystallography, Russian Academy of Sciences, , Leninsky prosp. 59, Moscow, 119333, Russia

Version of record first published: 07 Oct 2011

To cite this article: L. M. Blinov, V. V. Lazarev, S. P. Palto & S. G. Yudin (2011): Ferroelectric Switching of Thin Langmuir-Blodgett Films of P(VDF-TrFE) Copolymer: Comparison with Liquid Crystal Switching, Molecular Crystals and Liquid Crystals, 549:1, 10-18

To link to this article: http://dx.doi.org/10.1080/15421406.2011.581120

Mol. Cryst. Liq. Cryst., Vol. 549: pp. 10–18, 2011
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.581120

Ferroelectric Switching of Thin Langmuir-Blodgett Films of P(VDF-TrFE) Copolymer: Comparison with Liquid Crystal Switching

L. M. BLINOV,* V. V. LAZAREV, S. P. PALTO, AND S. G. YUDIN

Shubnikov Institute of Crystallography, Russian Academy of Sciences, Leninsky prosp. 59, Moscow 119333, Russia

The switching of polarization in ferroelectric polymer films is traditionally explained in terms of nucleation and motion of domain walls although such walls have never been observed in polymer ferroelectrics. As an alternative, the Landau-Ginzburg theory of the coercive field seems to be appropriate for ultrathin (1–5 monolayer) films. Data on the switching dynamics in the ultrathin films are very scarce. In this work the experiments on the polarization switching in the 20–240 nm thick films prepared by the Langmuir-Blodgett technique had been carried out using triangular voltages of low frequency in order to separate capacitive and polarization components of the current. Then the results have been compared with the data on polarization switching in liquid crystalline, antiferroelectric Langmuir-Blodgett films. There is a striking similarity in the time dependences of repolarization current for two materials. Due to this, we tentatively suggest a switching mechanism based on the field-induced rotation of the polarization vector. The latter allows one to estimate the rotational viscosity coefficient of the ferroelectric polymer responsible for the energy dissipation.

Keywords Ferroelectricity; thin films; polymers; liquid crystals

PACS 77.80 Fm; 77.55.tf

1. Introduction

Ferroelectricity in polyvinylidene fluoride (PVDF) and its copolymers with trifluoroethylene (TrFE) is known since 1978 [1, 2] and this phenomenon has found application in many devices such as electromechanical transducers, hydrophones, detectors of infrared radiation, non-volatile memory, etc [3–5]. Thin film polymer ferroelectrics switch at lower voltages than crystalline materials do. On the other hand, they are convenient materials for studying fundamental aspects of low-dimensional ferroelectrics [6,7]. In the last few years we see a reviving of the interest in ferroelectric materials. There is an evident trend to hybridization of semiconductor and ferroelectric (especially polymer) materials in new electronic devices [8, 9].

Historically, the main attention has been paid to relatively thick films (1–10 μm) prepared mostly by spin-coating technique. Such films have mixed amorphous and crystalline phase and after stretching and annealing show quite a high spontaneous polarization (about

---

*Corresponding author. E-mail: lev39blinov@gmail.ru

$P_s = 0.1$ C/m^2 for P(VDF-TrFE) of 70/30 composition [10]). Langmuir-Blodgett (LB) films of the same polymer transferred from the water surface onto a solid substrate do not need stretching and have almost the same P_s with annealing at relatively low temperature of 120°C. They show clear transition from the paraelectric to the ferroelectric phase, ferroelectric switching, pyro- and piezoeffects even in films as thin as 1–2 monolayers [11]. Note that the interest to ferroelectricity in Langmuir-Blodgett films is continuously growing because this technique allows one to design nano-structured heterostructures having ferroelectric monolayers alternating with other functionalized monolayers based on magnetic materials, dyes, luminophores, biological molecules, etc. That monolayers can be located in the zone of a very strong built-in electric field and change their properties. In addition, the polymer structure allows the incorporation of almost any solid nanoparticles. Hence, one may look forward to new discoveries and technical applications in the areas of organic transistors [8], conductivity switchers [12], and all-organic, high-capacity data storage devices prepared by modern nano-imprinting techniques [13].

A mechanism of polarization switching in polymer ferroelectrics has not been well understood yet. The Landau-Ginzburg theory widely used in physics of crystalline ferroelectrics seems to work only for very thin polymer films (about 2–15 nm thick) [11]. In that case, the coercive field grows with decreasing thickness and reaches the theoretical maximum $E_c \approx P_s/\varepsilon_0$. For films thicker than 300 nm the coercive field is 1–2 orders of magnitude lower and the switching is traditionally explained in terms of a nucleation and growth of the field-induced domains with polarization parallel to the field. For abovementioned applications the intermediate range of film thickness (20–300 nm) is the most important, but the experimental results on polarization switching are rather scarce [14, 15]. As to the dynamic regime, the characteristic friction coefficients (viscosity), which determine the rate of polarization switching, depend dramatically on driving voltage and, in literature, may vary within many orders of magnitude.

In the present paper, the switching dynamics is studied for 20–250 nm thick ferroelectric LB films made of copolymer P(VDF-TrFE)(70/30). From the time dependences of the current density at different voltages $J(\mathrm{U}, t)$ we have estimated the coercive fields and switching times for films of different thickness and found a striking similarity in the shape of $J(\mathrm{U}, t)$ curves for the ferroelectric polymer and a liquid crystal, both prepared by the same LB technique [16, 17]. Based on this result we discuss qualitatively a possible mechanism for polarization switching.

2. Experimental

The films have been prepared using a Langmuir trough described earlier [18]. A weak (0.01 wt%) solution of the copolymer in cyclohexanone was spread onto the water surface at a temperature of $T = 20$–$22°$C to form a layer on the water surface. The layers were transferred onto glass substrates using a horizontal lift method [19] at a surface pressure of 4 mN/m provided by an automatically moving barrier. Bottom Al electrode in the form of a 1 mm stripe was evaporated on each substrate before the layer transfer. After formation of the multilayer polymer structure, the latter was annealed for 1h at $T = 110°$C and the top Al electrodes (typically three on each substrate) were evaporated. In this way, three capacitors of area $A = 1$ mm^2 have been formed on each substrate. Their capacitance C_p was measured for each element with a standard bridge at a low voltage of $U = 0.3$ V and the film thickness was calculated using known permittivity of the non-poled copolymer ($\varepsilon \approx 10$ at room temperature). From numerous measurements (dielectric, interferometric and

AFM) we concluded that each transferred layer is 2 ± 0.3 nm thick. Here we present the experimental results obtained on the films of thickness $d = 10$ (only for $C_p(T)$ dependence) 30, 60, 120 and 240 nm. The temperature dependences of capacitance (at $U = 0.3$ V and frequency $f = 1$ kHz) show clear phase transition with a hysteresis typical of P(VDF-TrFE) copolymers. On heating the transition to the paraelectric phase is observed at 108°C ($d >$ 60 nm), 104°C ($d \approx 20$ nm) and 103°C ($d \approx 10$ nm).

To study the dynamics of polarization switching we used the repolarization current technique with a triangular waveform of the applied voltage at quite low ($f = 0.2$–10 Hz) frequencies. The triangular voltage pulses have linear slopes with constant (positive or negative) derivatives. The latter allows an easier separation of the polarization current from rather trivial capacitive and resistive components especially pronounced in such thin films and not properly taken into account in earlier dynamic experiments. The current oscillograms have been recorded by a digital storage oscilloscope. For comparison, we present also current oscillograms obtained on the LB films of a liquid crystal showing polarization switching. That compound is formed by bent-shape molecules and, in the B2 phase, manifests either ferroelectric or antiferroelectric behavior depending on applied voltage.

3. Results and Discussion

Switching characteristics

Fig. 1 shows typical oscillograms of the current response to the voltage of triangular form at frequency $f = 0.2$ Hz applied to a 120 nm thick cell. For clarity we plot only one quarter of the full period of the voltage waveform. The contributions of both the resistive and capacitive components (about 10% of the total current) are subtracted and the area under each curve represents the double value of the switched polarization (from $-P_{\mathrm{sw}}$ to $+P_{sw}$). With increasing voltage from $U = 14$ V to 35 V, the current maxima are growing and shifted to shorter times. The maximum current density of this film follows voltage

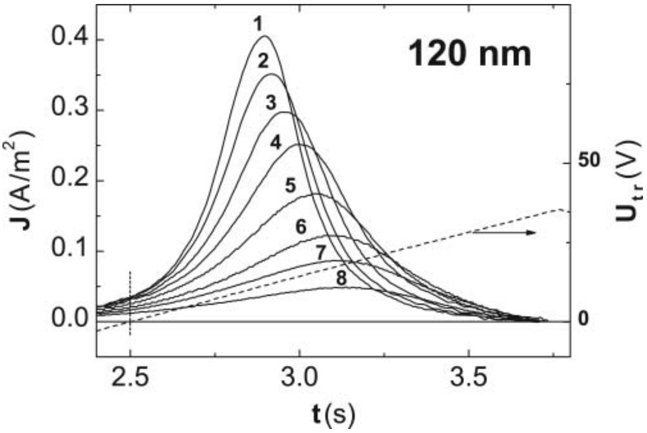

Figure 1. Switching current oscillograms for a 120 *nm*-thick LB film of P(VDF-TrFE) taken at varying electric field amplitudes of triangular form field E_m [in GV/m]: **1** – 0.33, **2** – 0.28, **3** – 0.25, **4** – 0.22, **5** – 0.19, **6** – 0.16, **7** – 0.15, **8** – 0.14 (frequency $f = 0.2$ Hz, only $\frac{1}{4}$ of the period T is shown, see the dash line for the voltage U_{tr}).

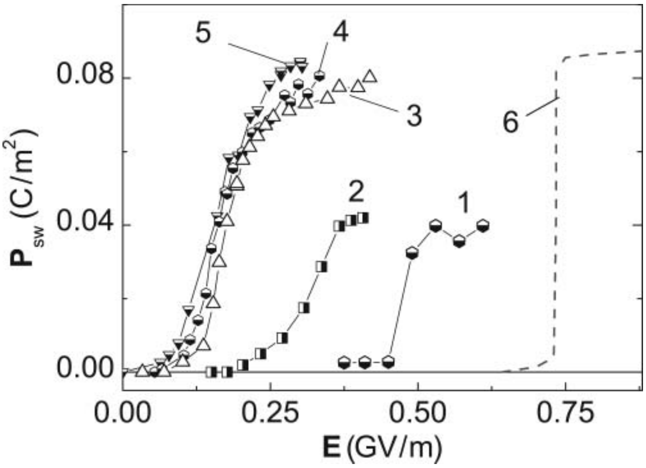

Figure 2. Switched part P_{sw} of the spontaneous polarization as a function of the applied electric field E for LB film of different thickness (lines + symbols)): $d = 20$ nm (curve 1), 30 nm (2), 60 nm (3), 120 nm (4), 240 nm (5). Calculated dependence of $P_{\mathrm{sw}}(E)$ for Landau-Ginsburg model with parameters $d = 120$nm, $\xi = 0.55 \cdot 10^9$ V·m·s/C (dash curve 6).

dependence of the type $J \propto (U\text{-}E_c d)$. Despite the maxima become narrower, the value of P_{sw} increases and then saturates at the level close to the spontaneous polarization $P_s \approx 0.08$ C/m^2 typical of such films [11]. Curve 4 in Fig. 2 shows such a field dependence of switched polarization $P_{sw}(E)$ obtained by integration of the current curves. When the field is cycled, $P_{\mathrm{sw}}(E)$ manifests a hysteresis with rather a low coercive field of $E_c \approx 0.1$ GV/m.

The triangular waveform of the non-destructive fields in the range of $E = 0.1$–0.7 GV/m was also applied to the films of other thickness. The corresponding repolarization current curves for films 30, 60 and 240 nm thick are presented in Fig. 3. The curves are similar to that shown in Fig. 1 and the values of the switched polarization also increase with voltage (see Fig. 2) although, in films thinner than 60 nm, P_{sw} cannot reach the value of $P_s \approx 0.08$ C/m^2 before breakdown of the film. The maximal switched polarization $P_{\mathrm{sw,max}}$ is shown in Fig. 4 as a function of the film thickness. The coercive field has also been measured: with increasing film thickness from 20 to 240 nm, it smoothly decreases and then stabilizes at the level of 0.1 GV/m as shown in Fig. 4 by curve E_c.

The switching times τ_{tr} (for triangular voltage) taken as a full width at half maximum (FWHM) do not vary very much with film thickness: for a given period of the field they range within 0.2–0.5 s for film thickness of 240–20 nm, respectively. As to the field dependence, the switching times approximately follow the law $\tau_{\mathrm{tr}} \propto (E\text{-}E_c)^{-1}$ that is very far from the exponential form characteristic of the domain nucleation mechanism. By the way, to our knowledge, the motion of domain walls has not been observed yet and the domain nucleation mechanism of polarization switching has not been unequivocally proved for the polymer films. Therefore, it is very difficult to interpret our data in terms of the domain nucleation mechanism and below we also try to apply the Landau-Ginzburg approach.

Comparison with Landau-Ginzburg (LG) Model

Earlier [11, 20] the LG model has been proved to be valid for films of thickness below 10 nm. Therefore, it is tempting to check the applicability of LG model to our present

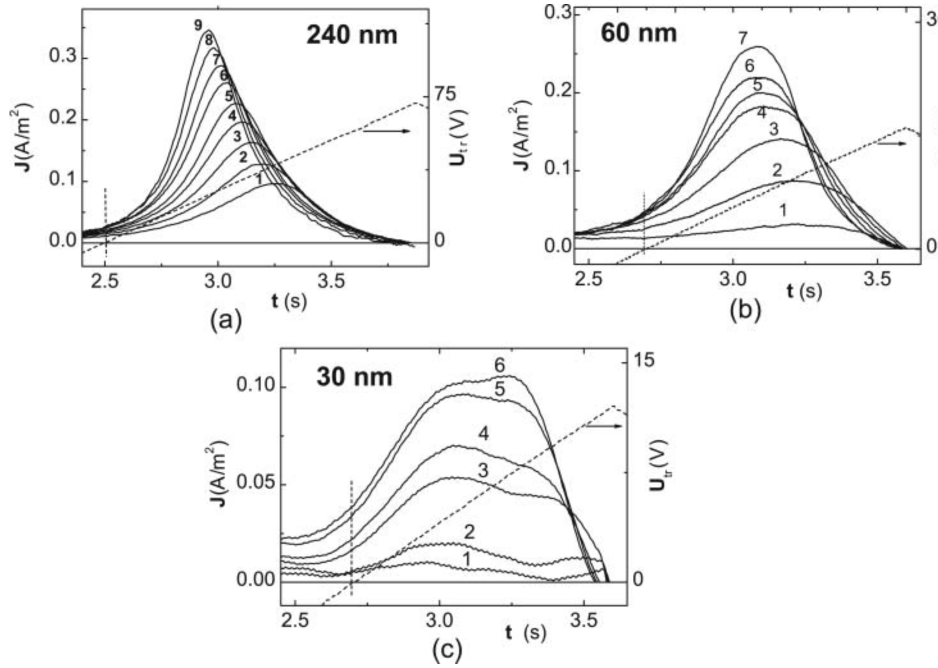

Figure 3. Time dependences of repolarization current for LB films 240 nm (**a**), 60 nm (**b**) and 30 nm (**c**) thick films for different voltages U_{tr} of triangular form. Amplitudes of U_{tr}: (**a**) $d = 240$ nm, f = 0.2 Hz, U_{tr} [in *V*]: 38.4 (curve **1**), 43.1 (**2**), 3 – 47 (**3**), 51.8 (**4**), 54.9 (**5**), 59.6 (**6**), 64.3 (**7**), 68.2 (**8**), 72.9 (**9**); (**b**) $d = 60$nm, f = 0.28 Hz, U_{tr} [in *V*]: 7.5 (curve **1**), 9.3 (**2**), 11.8 (**3**), 13.8 (**4**), 15.5 (**5**), 16.4 (**6**), 18.2 (**7**); (**c**) $d = 30$nm, f = 0.28 Hz, U_{tr} [in *V*]: 7 (curve **1**), 8.1 (**2**), 9.2 (**3**), 10.1 (**4**), 11 (**5**), 6 – 12.2 (**6**).

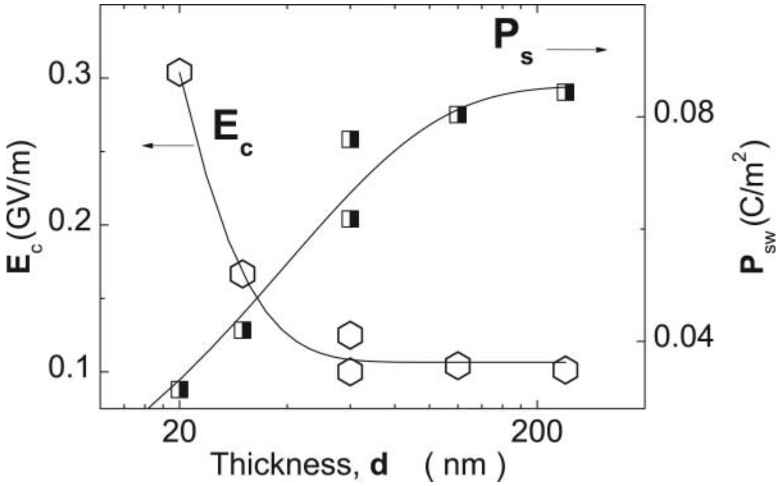

Figure 4. Thickness dependences of the maximum switched polarization P_{sw}(squares) and coercive field E_c(diamonds) for LB films in the range of ~20 – 240 nm. The solid lines are for eye guideline only.

experiment. The LG free energy expansion is given by $F(P,E) = \alpha(T - T_o)P^2/2 + \beta P^4/4 + \gamma P^6/6\text{-}EP$ where P is total polarization, T_0 is a second-order virtual phase transition temperature and α, β, γ are Landau coefficients measured earlier by our group for the same copolymer in vicinity of the phase transition: $T_0 = 74°\text{C}$, $a = 1.4{\cdot}10^8$ Jm/C^{2}K, $\beta = -3.9{\cdot}10^{12}$ Jm^5/C^4, $\gamma = 7.9{\cdot}10^{14}$ Jm^9/C^6. After minimization of $F(P,E)$ with respect to P we obtain $\alpha(T - T_o)P + \beta P^3 + \gamma P^5 = E$. The solution of this equation of state gives us a static hysteresis loop $P(E)$ [20]. The coercive field obtained from the loop in the LG model is about 0.65 GV/m at 25°C. This value agrees with coercive field of the films thinner than 10 nm but considerably exceeds any experimental values shown in Fig. 4.

Now we shall take formally the Landau-Khalatnikov equation with friction coefficient ξ responsible for energy dissipation $\xi(dP/dt) = -(\partial F/\partial P) = -[\alpha(T - T_o)P + \beta P^3 + \gamma P^5] + E$ and solve it for the linear-in-time field $E(t) = -E_m + 4E_m(t/\Lambda)$ corresponding to our triangular voltage form of period Λ. The repolarization current density necessary for comparison with experiment is given by $J = dP/dt$. The result of the numeric solution of the equation is shown in Fig. 5. In calculations, we used the same Landau parameters α, β, γ, T_0 [20], $T = 25°\text{C}$, the field of amplitude $E_m = 1.4$ GV/m (2.15 times exceeding the coercive field) and $\Lambda = 3.6$ s corresponding to experimental value of frequency $f = 0.28$ Hz. The friction coefficient ξ was varied in the limits (1–30) $\cdot\, 10^8$ V·m·s/C. Lower friction coefficients would give us too high and too narrow current peaks that is unrealistic, but higher coefficients ξ would result to incomplete switching for experimental values of the field period. For example, a curve for $\xi = 4 \cdot 10^{10}$ V·m·s/C, that is the value found in [15] would manifest no maximum within the time period of 3.6 s.

It is well seen in Fig. 5 that the switching has very sharp threshold with a coercive field of 0.75 GV/m, that is an order of magnitude higher than in experiment. In Fig. 2 (curve 6) we have also presented a model dependence of the switched polarization for a 120 nm thick film at some intermediate value of $\xi = 5.5 \cdot 10^8$ V·m·s/C. It is evident that this curve is very far from the experimental curve 4 for the same thickness film. The amplitudes of the calculated current density also strongly differ (one order of magnitude larger) from the

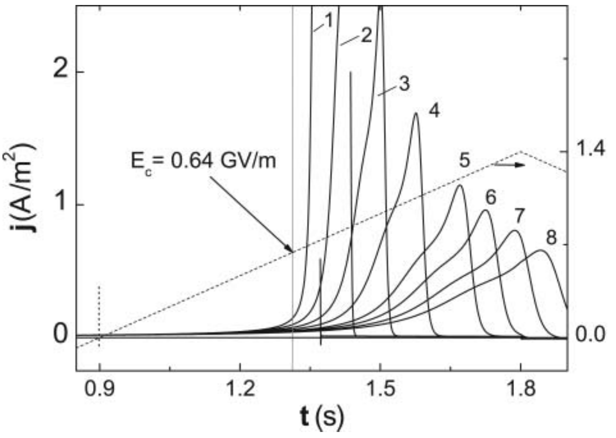

Figure 5. Solutions of the time dependent Landau-Khalatnikov equation. Evolution of repolarization current in triangular field of amplitude $E_m = 1.4$ GV/m and period $\Lambda = 3.6$ s with variable friction parameter ξ in units [Vms/C]: $1 \cdot 10^8$ (curve 1), $3 \cdot 10^8$ (2), $6 \cdot 10^8$ (3), $1 \cdot 10^9$ (4), $1.6 \cdot 10^9$ (5), $2 \cdot 10^9$ (6), $2.5 \cdot 10^9$ (7), $3 \cdot 10^9$ (8).

experimental values and we conclude that the Landau-Ginzburg model is hardly applicable to our P(VDF-TrFE) films of thickness 20–250 nm.

An Analogy with Liquid Crystalline LB Films

Looking at the whole picture of the polarization switching we see that the current curves for all samples have common features: a bell shape without distinct threshold and low coercive field (it means that the *P-E* hysteresis loop is rather narrow and tilted from the vertical *P*-axis). Earlier we studied 60–90 nm thick Langmuir-Blodgett films of a ferroelectric liquid crystal (tetradecyl homologue of 4-chloro-1,3-phenylene bis-[4-(4-*n*-alkylphenylimino)benzoates] for brevity THB) [16, 17] and observed the voltage and time dependences of repolarization currents very similar to those shown in Figs. 1 and 3. It is instructive to look at Fig. 6 showing repolarization current oscillograms for a film of liquid crystal compound THB in the B2 phase. The compound was dissolved in chloroform and spread over water surface. Then the surface layers were transferred onto substrates supplied by Al electrodes. At room temperature the transferred multilayers are in the crystalline, electrically inactive phase. The top Al electrodes were evaporated and capacitors formed as explained in the experimental part. Upon heating the material undergoes into the anti-ferroelectric B2 phase (within $T = 68$–$127°C$) and manifests the switching of spontaneous polarization between two field-on ($\pm P_s$) ferroelectric states accompanied by repolarization currents. The double peak curve is a signature of antiferroelectric switching. Note that, in ferro- and antiferroelectric liquid crystals, polarization vector $\mathbf{P_s}$ is rotated under the action of field torque $\mathbf{P_s} \times \mathbf{E}$ that, in turn, causes the director rotation. For reasonably high fields this torque is balanced solely by the viscous torque and one can find the rotational viscosity $\gamma_1 = AP_{sw}^2 E_{\mathrm{Im}}/I_m$ of the material [21].

For the curve corresponding in Fig. 6 to $U_m = 10$ V, the maximum current density $J_m = I_m/A = 2$ A/m^2 (for the right shoulder of the curve) located at $t = 23$ ms where the positive field $E_{\mathrm{Im}} = 1\mathrm{V}/90\ \mathrm{nm} = 0.011$ GV/m. Then with experimental values of $P_0 \approx 2 \cdot 10^{-3}$ C/m^2

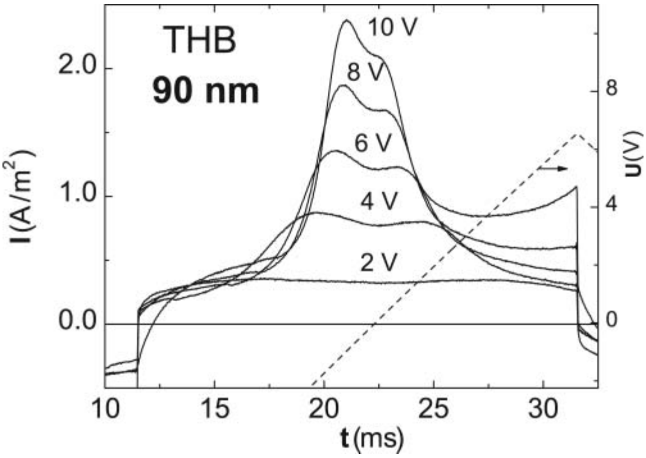

Figure 6. Repolarization current curves measured on the 90 nm thick LB film of THB compound at 75°C. The triangular voltage increases within a half-period from - U_m (at $t = 12$ ms) to + U_m (at $t = 32$ ms) with $U = 0$ at $t = 22$ ms. The amplitude of triangular voltage U_m of frequency 25 Hz is shown at the curves.

we find the rotational viscosity in the 90 nm thick LB film $\gamma_1 \approx 22$ Pas. This value is approximately an order of magnitude larger than the bulk rotational viscosity of the same material [22]. The characteristic relaxation times (approximately corresponding to the cell reaction on the voltage step E) may be estimated by a simple formula $\tau \approx \gamma_1/P_sE$. In the case under discussion $E \approx 10\text{V}/90$ nm ≈ 0.11 GV/m and $\tau \approx 0.15$ ms.

Since the bell-shape shape of the repolarization current curves for ferroelectric (Fig. 1) polymer and liquid crystal THB (Fig. 6) are very similar it is very tempting to imagine that, in our ferroelectric polymer, the $\mathbf{P}_s$ vector also rotates by the field with some friction (viscosity). At the microscopic level such model would agree with the infrared dichroism [5] and tunnel microscopy data [23] showing rotation of the CF_2 dipolar groups about the polymer chains under the field influence. In frame of this model and using the same technique [21] we have estimated a “viscosity for rotation of $\mathbf{P}_s$” in the polymer material P(VDF-TrFE) (70/30): $\gamma_1 \approx 0.5$ MPas. Needless to say that the value of γ_1 has nothing in common with the flow viscosity (or creep coefficient) of polymers. We can also estimate the friction coefficient $\xi = \gamma_1/P_s^2 = 8{\cdot}10^7$ V·m·s/C that is essentially smaller than the values estimated with the Landau-Ginsburg approach for similar films [15]. The characteristic time of the polymer reaction to the step voltage may also be estimated using $P_s = 0.08$ C/m^2 and $E = 0.25$ GV/m (see Fig. 2): $\tau \approx \gamma_1/P_sE \approx 25$ ms (typical value).

Conclusion

In conclusion, we have studied the dynamics of polarization switching in thin Langmuir-Blodgett films of ferroelectric copolymer P(VDF-TrFE) (composition 70/30) having thickness in the range of 20–250 nm. It is an intermediate range between the ultrathin films, whose properties may be understood in terms of the Landau-Ginzburg model of ferroelectricity, and rather thick spin-coated films, in which the switching process is considered as domain nucleation and growth phenomena. We used a repolarization currents technique with a triangular waveform of the applied voltage at low frequencies. The latter allows easier separation of the polarization current from rather trivial capacitive and resistive components especially pronounced in such thin films. From the time dependences of the current density at different voltages $J(U, t)$ we have estimated the coercive fields and switching times for films of different thickness. The results of our measurements show that neither the Landau-Ginzburg nor domain nucleation models are compatible with experimental data. On the other hand, we have found a striking similarity in the shape of $J(U, t)$ curves for the ferroelectric copolymer and an antiferroelectric liquid crystal, both prepared by the same LB technique. Therefore, we have come to the earlier idea [24] that the switching of ferroelectric polymer films may be related to the field rotation of the macroscopic polarization vector in visco-elastic media such as liquid crystals or other soft materials. More recently we have developed the corresponding theoretical model [25].

Acknowledgements

The work is supported in frame of a scientific program of the Physical Department of Russian Academy of Sciences.

References

[1] Keppler, R. G. & Anderson, R.A. (1978). *J. Appl. Phys.* **49**, 1232.
[2] Naegele D. & Yoon, D.Y. (1978). *Appl. Phys. Lett.* **33**, 132.

[3] Lovinger, A.J. (1983). *Science* **20**, 115.

[4] Wang, T.T., Herbert, J.M. & Glass, A.M. (Eds.). (1988). *The Applications of Ferroelectric Polymers*, Chapman and Hall: New York.

[5] Keppler, R.G. (1995). *Ferroelectric Polymers (chemistry, physics and applications)*, Nalwa, N.S. (Ed.), Marcel Dekker: New Yourk.

[6] Palto, S., Blinov, L., Bune, A., Dubovik, E., Fridkin, V., Petukhova, N., Verkhovskaya, K., Yudin, S. (1995). *Ferroelectric Lett.* **19**, 65.

[7] Bune, A.V., Fridkin, V.M., Ducharme, S., Blinov, L.M., Palto, S.P., Sorokin, A.V., Yudin, S.G. & Zlatkin, A. (1998). *Nature* **391**, 874.

[8] Naber, R.C.G., Tanase, C., Blom, P.W.M., Gelink, G.N., Marsman, A.W., Touwslager, F.J., Setayesh, S. & De Leeuw, D.M. (2005). *Nature Materials* **4**, 243.

[9] Stolichnov, I., Riester, S.W.E., Trodahl, H.J., Setter, N., Rushforth, A.W., Edmonds, K.W., Campion, R.P., Foxon, C.T., Gallagher, B.L. & Jungwirth, T. (2008). *Nature Mater*. **7**, 464.

[10] Furukawa, T. (1989) *Phase Transitions* **18**, 143.

[11] Ducharme, S., Fridkin, V.M. & Palto, S.P. (2002). In: *Ferroelectric Thin Films Materials.* Nalwa, H. S. (Ed.), Vol. 3: *Ferroelectric and Dielectric Thin Films*. Chapter 11, Academic Press: San Diego, 47.

[12] Asadi, K., De Leeuw, D.M., De Boer, B., & Blom, P.W.M. (2008). *Nature Mater.* **7**, 547.

[13] Hu, Z., Tian, M., Nysten, B. & Jonas, A.M. (2009). *Nature Mater.* **8**, 62.

[14] Kimura K. & Ohigashi, H. (1986). *Jap. J. Appl. Phys.* **25**, 383.

[15] Vizdrik, G., Ducharme, S., Fridkin, V.M., & Yudin, S.G. (2003). *Phys. Rev, B* **68**, 094113(1–6).

[16] Blinov, L.M., Lazarev, V.V., Geivandov, A.R, Palto, S.P., Yudin, S.G., Pelzl, G. & Weissflog, W. (2005). *Appl. Phys. Lett.* **87**, 241913.

[17] Blinov, L.M., Palto, S.P., Lazarev, V.V., Geivandov, A.R. & Yudin, S.G. (2006). *Kristallografiya*, **51**, 898. [*Crystallography Reports*, **51**, 843(2006)].

[18] Yudin, S.G., Palto, S.P., Khavrichev, V.A., Mironenko, S.V. & Barnik, M.I. (1992). *Thin Solid Films 210/211*, 46.

[19] Langmuir, I. & Schaeffer, V.J. (1938). *J. Am. Chem. Soc.* **60**, 1351.

[20] Ducharme, S., Fridkin, V.M., Bune, A.V., Palto, S.P., Blinov, L.M., Petukhova, N.N. & Yudin, S.G. (2000). *Phys. Rev. Lett.* **84**, 175.

[21] Escher, C., Geelhaar, T. & Böhm, E. (1988). *Liq. Cryst.* **3**, 469.

[22] Blinov, L.M., Barnik, M.I., Soto Bustamante, E., Pelzl, G. & Weissflog, W. (2001). *Phys. Rev. E* **67**, 121706.

[23] Cai, L., Qu, H., Lu, C., Ducharme, S., Dowben, P.A. & Zhang, J. (2004). *Phys. Rev. B* **70**, 155511.

[24] Geivandov, A.R., Palto, S.P., Yudin, S.G. & Blinov, L.M. (2004) *Zh. Eksp. Teor. Fiz.* **126**, 99–112 [JETP **99**, 83–94 (2004)].

[25] Lazarev, V.V., Blinov, L.M., Palto, S.P. & Yudin, S.G. (2010). *Phys. Rev. B* **82**, 134122.