Modeling of processes of near-electrode polarization in polymer films

Margarita E. Borisova

Abstract: **-** In this article the results of measurements of ramp and reverse voltage I-V characteristics in thin polymer films and in polymer blends at high temperature are presented. The experimental data were analyzed on the basis near-electrode polarization models by using of mathematical modeling. The analytic equations for calculation of the charge carrier mobility were received. It is established the ionic nature of charge carriers in polymer films at high temperature. The distributions of electrical field and potential were calculated.

Keywords: **-** polymer films, nonlinear effects, polarization, charge mobility, temperature dependence.

I Introduction

Different dielectric materials may be used as electrical insulation and as active dielectrics. In both cases it is very important to know the characteristics and nature of electro-transfer in dielectrics. There are the following methods of investigation of these effects in dielectrics, for example in thin polymeric layers:

-charging and discharging currents,

- discharging and restored voltages;

- ramp voltage and reverse voltage I-V characteristics;

- thermally stimulated polarization (TSP) and depolarization (TSD) currents and voltages.

The nonlinear polarization phenomena in thin polymer films (PETF, PVDF, ABC, PC) and in different blends (TPU/SAN) are discovered by measurements of the ramp voltage and reverse voltage I-V characteristics after polarization of samples under the action of voltage $-U_p$ during time t_p at high temperature T_p. The appearance of maxima on I(U) and I(t) curves are related to presence in film of charge carriers for wich blocking contact between dielectric and electrodes occurs [1-6]. In this case the charge carriers move from one electrode to another in every cycle of measuring U(t) without discharging on electrodes.

The results of investigation of ramp voltage and reverse voltage characteristics and there theoretical analysis can give us the information of charge carrier mobility that determine of material property used in electric technics and electronics [7].

M.E.Borisova is with St.Petersburg State Polytechnical University, 195251 Saint Petersburg, Russia(email: vladimirl.borisov@gmail.com)

II. Experimental

For measurement of reverse voltage I-V characteristics after polarization of the sample the voltage was abruptly changed from $-U_p$ to U_r (Fig.1a).

The ramp voltage I-V characteristics were measured by linearly rising of voltage $U = \beta t$ (Fig.1b). In this case upon changing voltage U(t)

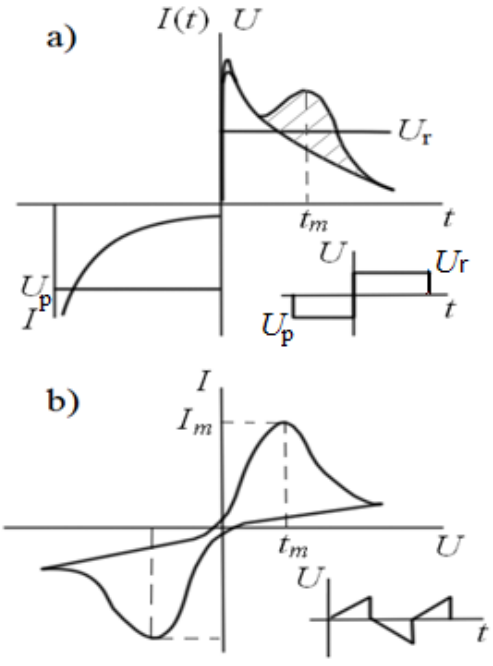

Fig.1 Reverse (a) and ramp (b) voltage curves

with the rate $dU/dt = \beta$ maximum of current is observed. The measuring of ramp voltage I-V characteristics may be reproduced at periodical change of voltage.

The results of measuring of reverse voltage I-V characteristics for PETF films at high temperature 170-200^{0}C are shown on Fig.2.

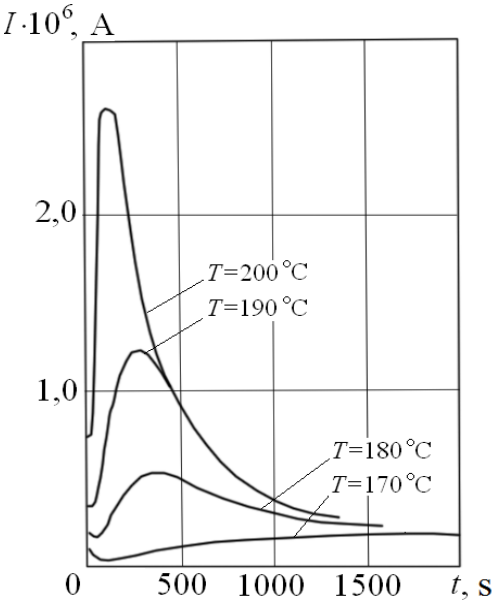

Fig.2 Reverse voltage I-V characteristics for PETF films (h=12 mkm)

It is demonstrated by Fig.2 that with rising of temperature the maximum of current I_m increases and the time of maximum t_m decreases.

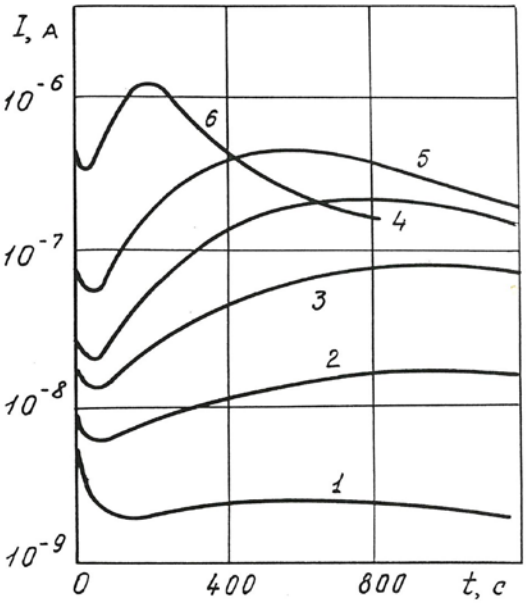

Fig.3 Reverse voltage I-V characteristics for PETF films (h = 6 mkm) for different U_r:
1 – U_r = 0, 2 – 1 *V*, 3 – 5 *V*, 4 – 10 *V*, 5 – 20 *V*, 6 – 50 *V*.
*T*p = 190 ^{0}*C*, *U*p = - 100 *V*

It is established that the time t_m grows with increasing the polarization voltage (Fig.3).

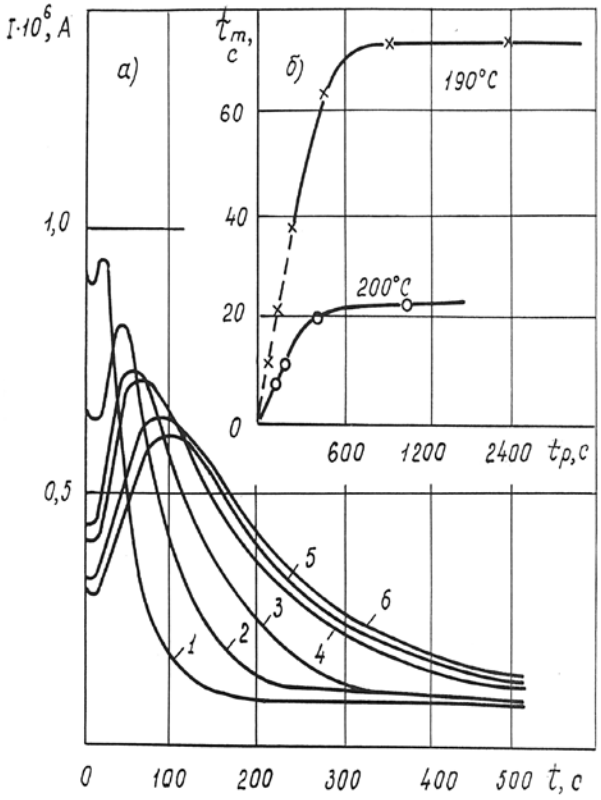

Fig.4 a) Reverse voltage I-V characteristics for PETF films for different polarization time t_p.
1 – *t*p = 120 *s*, 2 -240 *s*, 3 – 480 *s*, 4 – 900 *s*,
5 – 1800 *s*, 6 – 3200 *s*
b) Dependencies of the maximum position on the polarization time t_p . *T*p = 180^0*C*, *U*p = - 100 *V*, *U*r = 100 *V*.

The maxima of revers voltage characteristics shift to smaller time with increasing of the voltage U_r. The value of initial reverse current I at moment of the voltage inversion decreases with increasing the polarization voltage U_p and with increasing the time polarization t_p of the sample.

With raising of $-U_p$ and t_p the net charge Q increases. The value of Q is determined as an integral under the curve I(t).

However upon further increase in U_p and t_p the charge Q, t_m, $I_{rev}(t)$ and I(0) are stabilized.

The analogous changes are observed for ramp voltage I-V curves upon variation of parameters: $-U_p$, t_p, T and β. It is established that at constant temperature T the maximum on curves I(U) shifts to high value U_m or to lower $t_m = U_m/\beta$ upon an increase in the rate of the voltage variation $\beta = dU/dt$.

The value I_m increases with raising the voltage increase rate β [8]. The current at maximum I_m increases and position of the maximum shifts to region of lower values of U with increasing average electrostatic field E = -U/h.

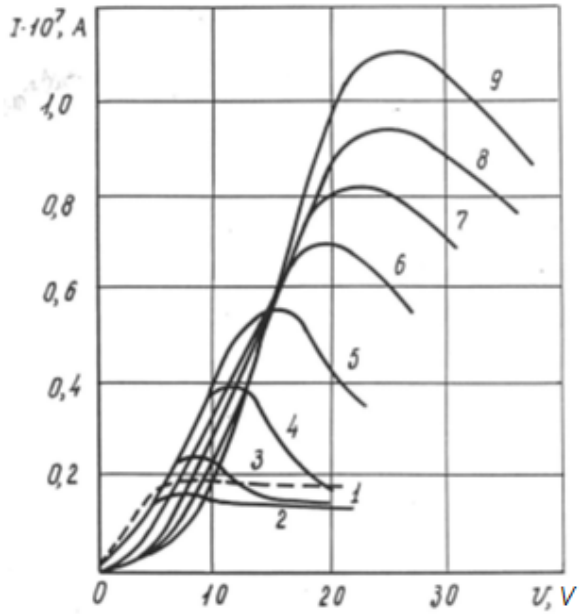

Fig.5. The ramp voltage I-V characteristics for different of time polarization t_p:
1- 0 *s*, 2 – 15 *s*, 3 – 30 *s*, 4 – 60 *s*, 5 – 120 *s*, 6 – 240 *s*, 7 – 480 *s*, 8 – 960 *s*, 9 – 1920 *s*.
Тизм = 190^0*C*, *Tp* = 190^0*C*, *Up* = 100 *V*

As in the case of reverse current I_{rev} the value ramp current (I_m) and the position of maximum (U_m, $t_m = U_m/\beta$) depend on polarization regime, i.e. on the values $-U_p$, t_p (Fig.5).

With raising temperature T at constant value of β the maximum of the ramp voltage I-V characteristics shifts to lower value U_m, i.e. to lower $t_m = U_m/\beta$. The value of current in maximum increases. The typical results of these measurements are shown on Fig.6.

Dielectrics measurements by means of thermally stimulated depolarization currents (TSDC) and reverse I-V characteristics were used to study the carrier mobility and polarization phenomena in blends of thermoplastic polyurethane (TPU) and styrene-acrylonitrile copolymer (SAN)with different SAN contents.

The reverse voltage I-V characteristics were measured for polymer blends at high temperatures of 120-160 ^{0}C. The choice of U_p and U_r was determined by the sample conductivity. The curves of reverse voltage characteristics have maxima which indicate

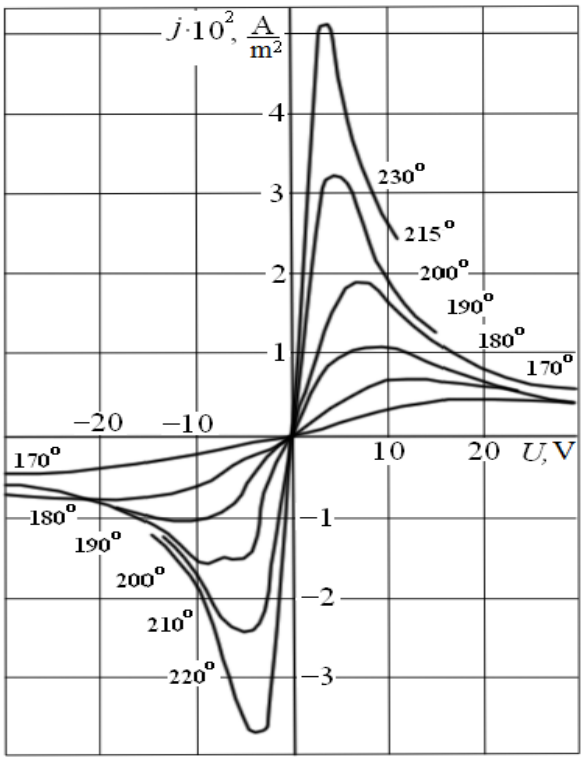

Fig.6.The ramp voltage I-V characteristics by different temperature (β = 18 mV/s).

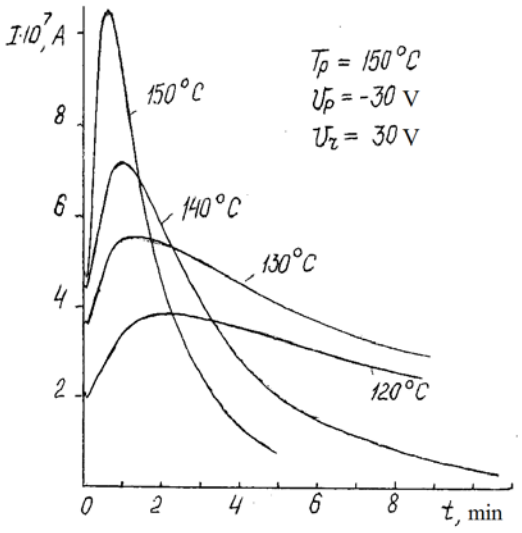

Fig.7.The reverse voltage I-V characteristics measured on 50/50 TPU/SAN blend.

the nonlinear effect of electro transfer. These characteristics for the blend 50/50 are presented on Fig.7.

With increasing temperature the peaks shift to shorter times. The analysis of I-V characteristics was made by the assumption that at relatively high temperatures the contact between electrodes and sample

is blocking for the carriers which provide the current through the volume of the sample.

By the method of thermally stimulated depolarization currents it was shown that in the high temperature range a hetero-charge is accumulated in the sample of blends TPU/SAN. On the TSDC thermo-grams we observe one peak which is related to the hetero-charge relaxation (Fig.8). We may assume that the hetero-charge accumulated near the blocking electrode. Fig.8 shows that the maximum of TSDC curves shifts to lower temperature within increasing TPU content in the blend. This is in agreement with an increase in the film conductivity [9].

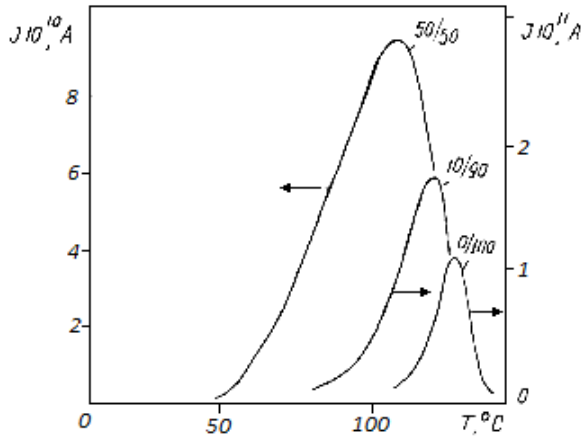

Fig.8 High temperature range TSDC thermo-grams measured on 50/50, 10/90 and 0/100 TPU/SAN blends.

III. Theoretical Analysis

The experimental results for thin polymer films obtained by us fully correspond to nonlinear theory of near-electrode polarization. Mathematic modeling of nonlinear elements was examine in work [10], [11].

The theoretical analysis of the experimental results was usually based on the assumption that contacts between electrodes and dielectric are blocking for the carriers which provide the current through the bulk of polymer. The simple analysis of ramp and reverse curves on the base of near-electrode polarization model did not take into account the carrier diffusion. It was assumed that sample of the dielectric polymer material comprises the charge carriers of one sign and fixed charge of another sign distributed uniformly in a bulk of polymer $\rho = -\rho_f = \rho_0$. We propose the model in which the carriers concentration in the initial state is equal n and the net charge of carriers per unite area is Q = n e h. This charge in the initial state of the dielectric is compensated by the fixed charge Q_f which is caused by the charge of shallow traps. These traps are immobile in the electrical field and $Q_f = - Q$. We assume that in the polarized dielectric sample the part of volume is free of carriers and this part possesses only the charge of immobile traps.

To determine of charge carrier mobility were analyzed the ramp and the reverse curves. The problem may be reduced to the solution of the equations of boundary moving for charge cloud x_1 and x_2. The schematic image of charge and electrical field distributions in the sample are presented on Fig.9.

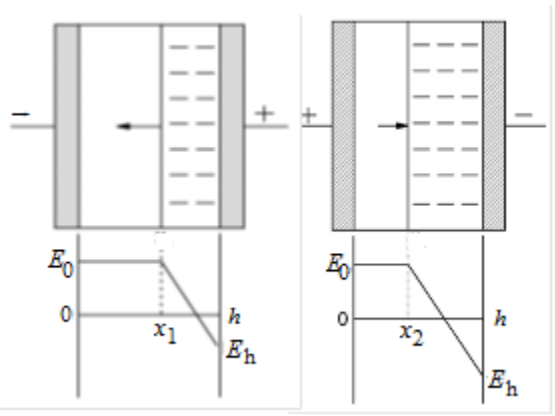

Fig.9 The schematic image of model

Taking into account of expression $De\dfrac{\partial n}{\partial x} = 0,$

$$Q_f = -Q = -neh, \quad \frac{dE}{dx} = \frac{\rho_f}{\varepsilon\varepsilon_0}$$

the velocity of boundary moving may be expressed by following formulae:

$$\frac{dx_1}{dt} = \mu E_1 = -\mu\left[\frac{U}{h} - \frac{Q}{2\varepsilon_0\varepsilon h^2}\left(h - x_1\right)^2\right] \quad (1)$$

$$\frac{dx_2}{dt} = \mu E_2 = -\mu\left[\frac{U}{h} - \frac{Q}{2\varepsilon_0\varepsilon h^2}x_2^2\right] \quad (2)$$

The current in circuit for two cases is determined by equations

$$j(t) = Q\frac{x_1}{h}\frac{dx_1}{dt}, \quad j(t) = Q\frac{h - x_2}{h^2}\frac{dx_2}{dt} \quad (3)$$

The system of equations (1 – 3) was solved by as on basis of numerical methods. The calculated curves j(t) have maxima as experimental curves. It was established that current maxima correspond to moment when the boundary x_1 achieves of electrode.

From comparison of experimental ramp and reverse I-V characteristics and theoretical [12] curves we obtained the following equations for calculating of the carriers mobility μ.

From the reverse voltage I-V characteristics we calculated the carrier mobility μ by the approximate formulae

$$\mu = j_m\frac{h^2}{U_r Q} \quad \langle for\ U = U_r \rangle \quad (4)$$

$$\mu = j_m \frac{h^2}{U_m Q} \quad \langle for\ U = \beta t \rangle$$

where h is the film thickness, U_r – is the reverse voltage, t_m – is the peak time, Q - is the total charge in external circuit and j_m- is the peak current. The values of μ calculated from these equations were found to be close

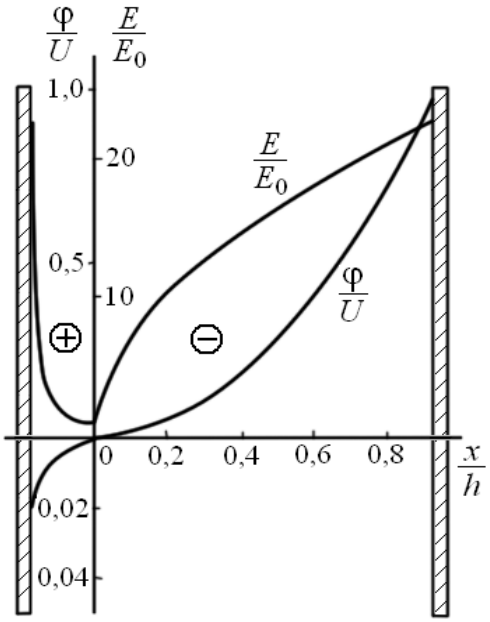

Fig.10 The distribution of electrical field E and potential φ for the dielectric model with one type of carriers and $\rho = -\rho_f$.

to each other. The value μ calculated from eq.4 for 50/50 TPU/SAN varies from 1.2×10^{-12} $m^2/V \cdot s$ at T = 120^0C to 4.16×10^{-12} $m^2/V \cdot s$ at T = 150^0C.

The value of Q may be evaluated from experimental data. The carrier mobility follows Arrhenius behavior with temperature. From the Arrhenius plot we obtain the activation energy of the carrier mobility equal to 0.65 eV. This value is very close to the conductivity activation energy, which was found to be E_a = 0.70 eV. Taking into account the small value of μ we may assume that ionic conductivity in TPU/SAN blend is predominant at high temperatures..

The values of μ calculated for PET films varied from $1{,}5 \times 10^{-16}$ to 4×10^{-14} $m^2/V \cdot s$. at temperature interval 100 - 200^0C.

Such values of mobility are typical for ionic charge carriers or for electron carriers moving with strong retraping.

The correct analysis of the ramp and reverse curves on the basis of considered above model may be fulfilled by solution of the system differential equation by using of numerical method:

$$\begin{cases} j = \mu\rho E - D\dfrac{\partial \rho}{\partial x} + \varepsilon_0 \varepsilon \dfrac{\partial E}{\partial t} \\ \dfrac{\partial \rho}{\partial t} = -\dfrac{\partial}{\partial x}\left(\mu\rho E - D\dfrac{\partial \rho}{\partial x} \right) \\ \dfrac{\partial E}{\partial x} = \dfrac{\rho + \rho_f}{\varepsilon_0 \varepsilon} \end{cases} \qquad (5)$$

with boundary condition

$$\int_0^h E dx = -U$$

$$j = \varepsilon_0 \varepsilon \frac{dE_0}{dt} = \varepsilon_0 \varepsilon \frac{dE_h}{dt}$$

where E_0 and E_h – electrical fields nearly electrodes x = 0 and x = h, ,$U = -U_r$ or $U = \beta \cdot t$.

For stationary state of near-electrode polarization the system of equation may be solved by analytical method. The results of calculation of potential and electrical field distributions in the stationary state are presented in Fig.10.

It is shown that at small value of U_p the charge is localized in a narrow near-electrode region of the dielectric forming the double electrical layer with charge on the electrode. The results of calculation show that with increasing voltage U_p the thickness of the near-electrode layer is sharply reduced.

.

IV. Conclusion

Near-electrode polarization in dielectrics takes place when contacts between electrodes and dielectric are blocking for the charge carriers which move through the bulk of dielectric. In this case charge carriers are accumulated near electrodes forming volume hetero-charge.

The reverse and ramp voltage I-V characteristics were measured by us for different polymer films and polymer blends at high temperature. It is established that the curves of these I-V characteristics have maxima of current.

At high temperature where maxima $I_{rev}(t)$ and $I_{ramp}(U)$ take place the hetero-charge is accumulated in polymer films.

The dependences $I_{rev}(t)$ and $I_{ramp}(t)$ were studied for different parameters of polarization: T_p, t_p, U_p. Experimental data obtained by us point to processes of nonlinear near-electrode polarization in films.

The charge carrier mobility μ was calculated from experimental curves of reverse and ramp voltage characteristics. The small values of μ point to ionic nature of conductivity that corresponds to results of other investigators [13].

The mobility of the charge carries is essential parameter determined the processes of electro transfer in dielectrics. The nature and mobility of charge carriers in polymers were studied by different methods in some works [14], [15], [16].

The ramp and reverse characteristics were analyzed on the base model of dielectric which content some charge of one sign and fix charge of another sign. It was received a few formulae for calculation of charge carrier mobility and total charge Q . The comparatively low values of mobility point to ionic type of charge carrier. However one cannot strike off and electron nature of carriers.

The distributions of electrical field E and potential φ were calculated by solution of the differential equation system with using of numerical method on the base correct model of dielectric. It was shown that charge is localized in narrow layer near electrode.

REFERENCES

[1] M. Onoda, H. Nakayama, K. Amakawa, «Transient current of plasticized polyvinylchloride,» *Japanese Journal of Applied Phys*ics,Vol.19, No.2, 1980, pp.381-382.

[2] K. Iida, H. Ishiguro, S. Nakamura, G. Sawa, M. Ieda, «Current peaks following voltage reversal in chlorinated polyethylene», *Journal of Applied Physics*, Vol.24, No.6, 1985, pp.666-668.

[3] S. Nakamura, G. Sawa, M. Ieda, «Electrical conduction of nylon 6 at the high temperature», *Japanese Journal of Applied Physics*, Vol.20, No.1, 1981, pp. 47-53.

[4] K. Miyairi, M. Ikeda, «Current peaks observed in polyethylene terephthalate films with linearly increasing voltage,» *Journal of Applied Physics*, Vol.19, No.6, 1980, pp.1067-1071.

[5] K. Miyairi, M. Ikeda, «Investigation of current-voltage characteristics in polymers by new method,» ,3rd Int.conf. Dielec. mater.,meas. and appl. Birmingham, pp.314-317, 1979, London-New York.

[6] M.E.Borisova, O.V. Galjukov, S.N. Kojkov, «Nonlinear effects of electrotransfer in polymer films,» *Electrotechnica*, No.7, 1991, pp.69-71.

[7] V. Sverdlov, J.Ghosh, D. Osintsev, S. Selberherr, «Modeling silicon spintronics», Book of Abstract 2014 International Conference of Mathematical Models and Methods in Applied Sciences (MMMAS 2014), Saint Petersburg, Russia, Sept.23-25, 2014, p.78.

[8] M.E.Borisova, O.V. Galjukov, S.N. Kojkov, «The migratory polarization in polymer and current maxima of dynamic current-voltage characteristics,» *Izvestiya of high educational school. Physics*, No.8, 1988, pp. 29-34.

[9] A.Kanapitsas, P. Pissis, A. Garcia Estrella. *European Polymer Journal*, Vol.35, 1999, p.923.

[10] N.Korovkin, J.Nitsch, E.Solovyeva, Examination of the demodulation effect of two-tone disturbances of nonlinear elements. Advances in Radio Science, Vol.2, No.2. 2004. p.51.

[11] G. Silkina, Mathematical modeling as analytical instrument of research of innovative processes, Book of Abstract 2014 International Conference of Mathematical Models and Methods in Applied Sciences (MMMAS 2014), Saint Petersburg, Russia, Sept.23-25, 2014, p.40.

[12] M.E.Borisova, O.V. Galjukov, «The investigation of the transfer parameters in polymer films by method of dynamic current-voltage characteristics,» *Izvestiya of high educational*
school. Physics, No.10, 1987, pp.101-106.

[13] Sh. Agrawal, R. Kumar, Preliminary study on blend based mixed ion-electron conductor-(PVA:PVK):CH_3COONH_4:ECsystem, International Journal of Materials Science and Application, V.3, No.4, 2014, pp. 129-136.

[14] R. Salichov, A. Lachinov, R. Rakhmeev, Electrical properties of heterostructure Si/poly(diphenilenephthalide)/Cu. Journal of Applied Physics, Vol.101, 2007, p.053706.

[15] V. Nikitenko, A. Tameev, A. Vannikov, A. Lachinov, H.Bassler, Bipolar space charge formation and svitching effect in thin polymer films. Applied Physics Letters, Vol.92, 2008, p.153307

[16] R. Salichov, A. Lachinov, Polymer thin film chemical sensors. In Book Advances in Chemical Sensors, Edited by Prof. Wen Wang, In Tech, 2012.