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Radiation induced transient currents in films of poly(arylene ether ketone) including phthalide moiety

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Abstract: Electrical properties of the thin films of poly(arylene ether ketone) copolymers (co-PAEKs) with the fraction of phthalide-containing units of 3, 5 and 50 mol% in the main chain were investigated by using radiation induced conductivity (RIC) measurements. Transient current signals and current-voltage (I-V) characteristics were obtained under exposing 20±25 thick films of the co-PAEKs to monoenergetic electron pulses of the energy ranged from 3 to 50 keV in the electric field ranged from 5 to 40 V/μm. The Rose-Fowler-Vaisberg semi-empirical model based on a multiple trapping formalism was used for an analysis of the RIC data and the parameters of the highly dispersive charge carrier transport were evaluated. The analysis revealed that charge carriers moved in isolation from each other and the applied electric fields were below the threshold field triggering the switching effect (a reversible high-to-low resistivity transition) in the co-PAEK films. It was also found that the co-PAEK films due to the super-linear I-V characteristics are highly resistant to electrostatic discharges arising from the effects of ionizing radiation. This property is important for the development of protective coatings for electronic devices.

Keywords: co-polymer; polyarylene ether ketones, switching effect, irradiation by electrons; small-signal regime; radiation induced conductivity; dispersive transport; carrier mobility.

1. Introduction

Intensive researches on the use of polymers as microelectronics elements are under way [1,2]. Thin films of polydiphenylterephthalide (PDP) are known to exhibit reversible electroresistive state switching (ERSS) called a switching effect [1,3]. In a strong electric field, the switching effect is of a sharp jump reversible transition of the polymer resistivity from a high-ohmic state to a low-ohmic state. ERSS is important for the development of next-generation non-volatile memory devices. A polymer material with the intrinsic switching effect would be of great interest because its properties can be adjusted over a wide range by fabrication techniques and modifications of the molecule structure.

The origin of the resistivity switching in the PDP thin films was explained by the transition of the conformation of the macromolecules between two stable states due to the reorganization of the phthalide moieties by the action of external electric field [1]. At the high resistance state, the charge carrier mobility in the PDP films was of the orders of 10⁻⁸ and 10⁻⁴ cm²V⁻¹s⁻¹ with a tendency to increase as the electric field approaches the threshold switching voltage to the low resistance state [4]. Similar charge mobility values were also demonstrated by a polyimide consisting phthalide moiety in the polymer unit [5].

There is still no generally accepted physical model describing the switching effect thin polymer films. This complicates the productive development of microelectronic devices, although the low
conduction switching thresholds in electric fields and the reversibility of these effects seem highly promising. Practically important field of application of such polymeric materials is obviously the protective coating of electronic devices. Film coating made of polymeric material that is capable of transporting charge carriers prevents the accumulation of charge when subjected to electron or ionizing radiation and thereby prevent subsequent electrostatic discharges leading to failures of electronic device.

Poly arylene ether ketones (PAEKs) possess reasonable electrophysical properties along with high thermal, chemical and mechanical resistance [6-10]. Thin films of PAEK co-polymers as well as the PDP thin films exhibit reversible ERSS [1, 11]. Therefore, varying the phthalide content of co-PAEKs, one can tune the electrical properties of the polymer films [11]. In this regard, a study of electrical conductivity in co-PAEKs with various content of phthalide fragments in the units is of a particular interest for revealing the ability to the resistivity switching in the films of the order of ten microns in thickness.

This article presents the results of the electronic transport investigation in films of co-PAEK with the various content of phthalide moiety using the enhanced radiation induced conductivity (RIC) measurement method combined with the time-of-flight technique (TOF) [12]. In this method, two types of charge introduction into the test sample are implemented: nearby the front electrode (as for the conventional TOF) and in the bulk of the polymer film (RIC). Exposing polymer films to monoenergetic electron pulses of the energy ranged from 3 to 50 keV allow us to investigate tens of microns thick films. The experimental approach for investigating the transport of charge carriers in the co-PAEK films is of particular interest in detecting the resistance of the co-polymer to electrostatic discharges due to ionizing radiation.

2. Experimental

2.1. Materials. Co-PAEKs shown in Fig. 1 were synthesized by polycondensation of 4,4'-difluorobenzophenone with dipotassium bisphenolates proceeding by the mechanism of nucleophilic substitution of activated halogen in the aryl dihalide analogously to the earlier described preparation of homopolymers [13]. The concentration of the bisphenols mixture was 0.5 mol per 1 liter of the solvent with K$_2$CO$_3$ being in the 30% excess. As an example, the procedure for the synthesis of co-PAEK (with a copolymer unit ratio of p:n = 0.5 : 0.5) based on 2,2-bis(4'-hydroxyphenyl)propane, 3,3-bis(4'-hydroxyphenyl)phthalide, and 4,4'-difluorobenzophenone was as following. 4,4'-Difluorobenzophenone (0.1 mol), 2,2-bis(4'-hydroxyphenyl)propane (0.05 mol), and 3,3-bis(4'-hydroxyphenyl)phthalide (0.05 mol), premilled freshly and calcined K$_2$CO$_3$ (0.13 mol), DMAA (200 mL), and chlorobenzene (100 mL) were loaded in an argon-blown four-necked flask equipped with a stirrer, an argon supply tube, and a system for azeotropic removal of water. The flask was heated on an oil bath whose temperature was increased from r.t. up to 185°C within ~0.5 h. After complete removal of an azeotropic chlorobenzene-water mixture, the synthesis lasted 7 h. The reaction mixture was cooled and dissolved in chloroform. The resulting solution was filtered from salts and washed by stirring with water many times. After evaporation of the chloroform solution at 25°C and drying by gradual increasing the temperature from 60 to 140°C over a period of 18 h and then at 160°C for 25 h, the co-PAEK was obtained as a film in yield of 99%. The reduced viscosity (η$_{red}$) determined for a solution of the polymer in chloroform (0.5 g/100 mL) at 25°C was 0.50 dL g$^{-1}$. The other synthesized co-PAEKs possessed high molecular weight and η$_{red}$ = 0.54 - 0.82 dL g$^{-1}$.

All the polymers are readily soluble in a wide range of solvents (dichloromethane, chloroform, sym-tetrachloroethane, THF, dioxane, cyclohexanone, m-cresol, DMF, DMAA, etc.). their films formed by drop cast from a solution are strong (the tensile strength was 77-85 MPa) and transparent in the spectral range of 400–1200 nm. In the studied co-PAEKs, the fraction of phthalide-containing units was n = 3, 5 and 50 mol%.
2.2. Methods. RIC measurements. The most valuable information has been obtained using 50 keV electrons (maximum range about 40 μm) in a pulse (1 ms) and continuous (exceeding approximately 0.1 s) irradiation modes while TOF application (electron energy 3-7 keV with their range being less than 1.5 μm) was unsuccessful due to co-PAEK electronic properties.

RIC irradiations of 50 keV electrons were normally incident upon polymer samples inside a vacuum chamber of the ELA-65 electron gun at room temperature only. The dose rate depth profile was typical for 50 keV electrons so that an average dose rate was estimated to be 2 times larger than at the front surface of a sample. RC time constant was about 1 ms.

All specimens 20 to 25 μm thick (40 mm in diameter) were supplied with evaporated Al electrodes 32 mm in diameter and 50 nm thick. Applied electric field was ranged from 20 to 40 V/μm. We used only just-prepared samples for each experimental run. RIC and TOF techniques have already been described in details [14, 15].

3. Results

We start with presentation of RIC pulse results which are most straightforward (Fig. 2). Pulse length was 1 ms and the flat top of the pulse extends from 100 s to the pulse end (RC time constant was 10 s). Irradiation was conducted in a small signal regime with no recombination present at any observation time.

The most important information from Fig. 2 is as follows. The maximum RIC happens at the pulse end and is equal to \( K_m = 1.7 \times 10^{-14} \Omega^{-1} \cdot m^{-1} / (\text{Gy/s}) \equiv F \cdot \text{m}^{-1} \cdot \text{Gy}^{-1} \) (the RIC per unit dose rate) which is a legitimate characteristic of a polymer at a small signal irradiation. It is seen that RIC rises with time slightly slowing down to the pulse end when its logarithmic slope \( \beta = d \lg \gamma / d \lg t \)
becomes equal to 0.15. After the pulse end, RIC falls rapidly during initial 500 s but then stabilizes at a falling rate $\beta_f = -\beta$, in our case $= 0.95$.

![Figure 3](image1.png)

**Figure 3.** The current-voltage ($I$-$V$) characteristic of co-PAEK films with the p/n ratio of 0.5/0.5.

We could see no traces of the transit time effects (the fact that $\beta_f$ is close to unity strongly hampers their observation (see later). By the way, $K_{rn}$ in PAEK happens to be 9 times smaller than in polystyrene in which transit time effects are also absent at this high field.

It could be seen that at this pulse length the delayed component of RIC ($\gamma_{rd}$) coexisting with the prompt ($\gamma_{rp}$) clearly dominates so that does not exceed $0.4 \times 10^{-14}$ F·m$^{-1}$·Gy$^{-1}$.

Figure 3 shows the $I$-$V$ characteristic of co-PAEK films with the p/n ratio of 0.5/0.5. The current of the radiation conductivity delayed component in relative units is measured along the ordinate axis.

We see that in contrast to $K_{rp}$, delayed component current and $K_{rd}$ strongly depends on the applied electric field $F_0$. In the field range 5 to 40 V/μm $K_{rd} \propto F^{1.7}$ thus testifying to the Onsager mechanism of the free charge carrier generation [16].

![Figure 4](image2.png)

**Figure 4.** RIC transient current taken in a small-signal irradiation. Dose rate 19 Gy/s, electric field 40 V/m, irradiation time 100s. The RIC rise is approximated with a dashed straight line having the same
slope (0.15) as the pulse irradiation at 1 ms (the transient curve is slightly distorted by rf-noise and the beam current instability).

An attempt to study charge carrier mobility directly using TOF technique as we did earlier with molecularly doped polymers failed as Fig. 2 shows: the current curve simply duplicated respective RIC curves producing no kinks on the current transients.

In principle, the above information quite suffices to construct mobility model in co-PAEK (see later) but to extend it to longer times, we supplemented our pulse RIC measurements with the long-term irradiations still in the small-signal regime (Fig. 4).

It is important that RIC show the same pattern of a rising current as observed during 1 ms pulse irradiation (slopes \( \beta \) are the same). More to that, extrapolation of RIC from 1 ms through the dead time gap to 0.1 s (opening time of a shutter) when an irradiation with a constant dose rate establishes itself \((2.8 \times 10^{14} \text{ F.m}^{-1}\text{Gy}^{-1})\) almost coincides with the measured one at 0.1 s \((3.1 \times 10^{14} \text{ F.m}^{-1}\text{Gy}^{-1})\) well within error bars (20 %). It follows that the delayed RIC rises according to a power law \( \gamma_d \propto t^{0.15} \) in a broad time range up to 100 s. As we will see below this fact allows a definitive conclusion about charge carrier transport in PAEK.

3. Discussion

To analyze the above RIC data, we used the Rose-Fowler-Vaisberg (RFV) semi-empirical model based on a multiple trapping formalism \([17, 18]\). The basic equations of the conventional one-carrier RFV model are as follows:

\[
\begin{align*}
\frac{dN}{dt} &= g_0 - k_r N_0 N, \\
\frac{d\rho}{dt} &= k_r N_0 \left[ \frac{M_0}{E_1} \exp \left( -\frac{E}{E_1} \right) - \rho \right] - \nu_0 \exp \left( -\frac{E}{kT} \right) \rho, \\
N &= N_0 + \int_0^\infty \rho dE.
\end{align*}
\]

at \( t = 0 \) both \( N_0(t) \) and \( \rho(E,t) \) are equal to 0.

By definition, the RIC is \( \gamma_d(t) = e\mu_0 N_0(t) \). Thus, system (2) refers to unipolar (by tradition, electron) conduction. Here \( N(t) \) is the total concentration of radiation-produced electrons (equal to that of holes), \( N_0(t) \) is the concentration of mobile electrons in extended states (in transfer band) with microscopic mobility \( \mu_0 \); \( g_0 \) is the generation rate of free charge carriers (assumed time and space independent during irradiation); \( k_r \) is the recombination coefficient of mobile electrons with immobile holes acting as recombination centers; \( k_r \) is the trapping rate constant; \( M_0 \) is the total concentration of traps exponentially distributed in energy \( E \) which is positive and taken downwards from the energy level of the transport band; \( E_1 \) is the parameter of the trap distribution; \( \rho(E,t) \) is the time dependent density distribution of trapped electrons; \( \nu_0 \) is the frequency factor; \( T \) is temperature; \( k \) is the Boltzmann’s constant and \( e \) is an elementary electric charge. Dispersive parameter \( \alpha \) which defines the major temporal features of the transient curves is equal to \( kT/E_1 \).

Also, \( \tau_0 = (kM_0)^{-1} \) is the lifetime of mobile electrons before trapping. Of course, \( g_0 \) is proportional to the dose rate \( R \), depending on the temperature and an applied electric field. In the case of hole conducting polymers the roles of electrons and holes are to be swapped.

In a small-signal regime Eqs. 1 simplify as recombination term in the first equation may be neglected. Now, the RFV model allows analytical solutions which show that the logarithmic slope \( \beta \) coincides with the dispersion parameter \( \alpha \) of the model. More to that, theory shows that the following relationship holds \((\alpha \leq 0.5, \text{vol 1})\):

...
The received results indicate that in the \(10^{13}\) transparent conductive polymer films, it is able to withstand electric fields of even \(10^{8}\) V/\(\mu \text{m}\) and room temperature. Taking \(\rho=1.2\), we immediately recover the triple product \(P=\mu_0\sigma_0\alpha\) which defines the expected time of flight through polymer film \((L\text{ is its thickness})\):

\[
K_{\text{id}}(t) \approx \eta_0 \mu_0 \tau_0 e(v_f t)^\alpha
\]

where, \(\eta_0 = g_0/R_0\) and \(\eta_0 = 10\rho G_0\), where \(\rho\) is a polymer density \((\text{g/cm}^3)\) and \(G_0\) is the yield of free charge carriers per 100 eV of absorbed energy. According to the Onsager mechanism this quantity is close to 0.8 at 40 V/\(\mu \text{m}\) and room temperature. Taking \(\rho=1.2\), we immediately recover the triple product \(P=\mu_0\sigma_0\alpha\) which defines the expected time of flight through polymer film \((L\text{ is its thickness})\):

\[
t_{\text{tr}} \approx (L/\rho L_{\alpha})^{1/\alpha}
\]

In our case, \(1/\alpha \approx 6.67\) so that taking \(t=0.1\) s and \(K_{\text{id}} = 3.1 \times 10^{-14} \text{ F m}^{-1} \text{ Gy}^{-1}\) we find \(P=4.4 \times 10^{-14}\) (in SI). As a result, an expected time of flight through the 20 \(\mu\text{m}\) thick co-PAEK film at an applied field \(F=40\) V/\(\mu\text{m}\) would be astronomically large \((10^{13})\) s. No wonder that our TOF experiment failed. Reducing sample thickness to 1 \(\mu\text{m}\) makes transit time much shorter \((2 \times 10^6\) s\) but still too large. In fact, one can speak about transit time effects only in polymer layers thinner than 0.1 \(\mu\text{m}\).

Thus, in about 20 \(\mu\text{m}\) thick films at electric fields of 5-40 V/\(\mu\text{m}\), the charge carrier transport is highly dispersive and the carriers exhibit low mobility. The received results indicate that in the studied range of electric field the increase in quantity of the co-PAEK units with the phthalide moiety from the p/n ratio of 0.97/0.03 to 0.5/0.5 did not lead to the noticeable RIC change within an experimental error. Therefore, in our experiments, charge carriers move in isolation from each other at electric fields, which are still insufficient for triggering the switching. Indeed, ultrathin films withstand electric fields of even \(10^8\) V/m. Such electric fields were not achievable in our experiments because a 20 \(\mu\text{m}\) polymer film underwent electrical breakdown. The very low mobility may be caused by geometric constraints associated with the arrangement of phthalide groups in the co-PAEK. The distance between the charge carriers within the phthalide monomer unit is much smaller than that between phthalide groups separated by an arylene monomer unit \(p\) (Figure 1). Thus, hopping of charge carriers between phthalide groups serving as charge transporting sites is difficult.

This consideration is consistent with the mechanism suggesting that the dielectric-to-conductive state switching occurs due to the formation of conductive channels in a polymer film [19]. In the RIC experiments at low electric field, lifetime of generated charge carriers \((\text{i.e. charge pairs (CPs)}\) is short because of their easy geminate recombination. At high electric field those CPs can be in a metastable energy state and the recombination is remarkably decreased, as evidenced by the experiment on delayed luminescence in a conjugated polymer. [20] This leads to an increase in concentration of CPs, needed to strong overlap of the Coulomb potentials for providing the high charge mobility within the conductive channels.

Another point is related to the film reaching pre-threshold state time. The co-PAEK \((p/n=0.5/0.5)\) were exploited in silicon solar cells as a transparent conductive polymer [11]. Yet, in our RIC measurements, the co-PAEK films did not switch from dielectric to conductive state within a time of the transient current observing. Thus, one may conclude that the switching of these co-PAEK films can occur for a much longer time than the duration of the transient RIC experiments.

Besides, the non-linearity of the \(I-V\) characteristics of the co-PAEK films shows that at strong pre-breakdown fields an increase of the super-linearity can be expected. At this condition, when the C-O bond in phthalide group will be broken [1], a transition from the transport of isolated (individual) charge carriers, which is observed in our experiments, to collective interaction with the above-mentioned conductive channel formation [19] can occur. In RIC experiments, charge carriers move in isolation whereas collective movements are observed in the switching effect. Therefore, we just start with the measurement of the charge carrier mobility. In order to continue the switching effect research in thin films of electroactive polymers, further setting of the experiment is necessary.

The increased stability of the co-PAEK films when exposed to ionizing radiation and their super-linear \(I-V\) curves result in to increased resistance of the films to electrostatic discharges. It is seen in Figure 3, as the electric field increases by 8 times, the current flowing through the sample and characterizing Maxwell’s relaxation time of the injected charge increases more than 30 times, which dramatically reduces the probability of reaching breakdown fields.
5. Conclusions

In this work, we have used the enhanced radiation induced conductivity (RIC) measurement method combined with the time-of-flight technique (TOF) in order to investigate the electron transport in films of co-polymers of poly arylene ether ketones (co-PAEKs). For the study, a number of co-PAEKs differing in the content of phthalide-containing units in the main chain (3, 5, and 50 mol%) have been synthesized and their 20 to 25 μm thick films have been prepared.

In the electric field \( F \) ranged from 5 to 40 V/μm, a strong non-linearity (super linearity) of current-voltage (\( I-V \)) characteristics with the relation \( K_{iR} \propto F^{1.7} \) has been observed in the co-PAEK films. Such \( I-V \) characteristic indicates that the free charge carrier generation obeys the Onsager mechanism.

The RIC measurements have shown that the charge carrier transport is strongly dispersive with low dispersive parameter \( \alpha = 0.15 \). The analysis of the experimental data in terms of the Rose-Fowler-Vaisberg model has revealed that transit time effects on the parameter are to be expected only in very thin polymer layers (less than 0.1 μm in thickness) even in strong electric fields of about 40 V/μm.

Within the used range of electric field, the increase in the concentration of phthalide-containing units in co-PAEKs from 3 to 50 mol% has not influenced the data on RIC in the all co-PAEKs. The finding points that in our experiments, charge carriers moved in isolation from each other and the range of the applied electric field was insufficient for triggering the switching effect in the co-PAEK films.

The type of ionizing radiation we have used affects electronic devices of spacecrafts operating in geostationary and highly elliptical orbits, especially during geomagnetic perturbations [21, 22]. We have shown that the co-PAEK films due to their super-linear \( I-V \) characteristics possess increased resistance to electrostatic discharges arising from the effects of ionizing radiation.

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