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Relaxation process at conductive poly(thiophene) and its poly(alkyl) derivatives : kinetics of electrochemical doping

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Summary

The kinetics of relaxation i.e. the kinetics of the doping process, have been investigated in poly(thiophene) and its alkyl substituted derivatives poly(3-methyl thiophene) and poly(3-octyl thiophene), by cyclic voltammetry. The polymer films, electrochemically deposited onto platinum and titanium electrodes, relax at various rates, depending on their structure and orientation in relation to the metal surface. The relaxation process is faster in polymers with longer alkyl chains.

Introduction

Relaxation processes in polymer materials are usually considered to be transitions to their equilibrium state, governed by internal forces. Due to the chain character of the macromolecules, these transitions are very slow processes and therefore are observed during the so-called relaxation time. Various relaxation phenomena in polymer materials e.g. mechanical, electrical, magnetic relaxation etc. have been identified [1].
Slow relaxation processes in conductive polymers, electrochemically synthesized onto metal substrates, have received considerable attention [2,3]. Odin et al. observed the relaxation phenomenon in polymer films that were maintained for some time at potentials corresponding to their neutral state [4]. The induced changes were successfully studied using the cyclic voltammetric method, by analyzing the first positive going cycle after the polymer film was kept in insulating state. The oxidation peak characteristics were found to obey the logarithmic low versus the wait time in poly(aniline) and poly(3-methyl thiophene) [5].
Different interpretations were proposed in relation to the relaxation phenomenon. According to one of them, the relaxation process is considered to be due to incomplete polymer matrix reduction [6], while the others suggest that the polymer film undergoes conformational changes during the switching process [7].
The aim of this paper is to describe the kinetics of the relaxation processes in three

polythiophenes: poly(thiophene), poly(3-methyl thiophene) and poly(3-octyl thiophene), as well as the influence of the structure, length of the side chain substituent and the nature of the metal substrate on the process.

Experimental

The starting monomers, thiophene, 3-methyl thiophene and 3-octyl thiophene (products of *Across Chemicals*) were used without further purification. The polymer films were prepared by electrochemical oxidation of monomers in a three-electrode, single-compartment cell. The films were grown potentiodynamically on platinum and titanium working electrodes with saturated calomel as reference and platinum as counter electrode. The solutions used for the preparation of films contained 0.1 M of the appropriate monomer with 0.1 M $LiClO_4$ in acetonitrile. The film thickness was controlled by the total charge Q_t involved during the electrochemical polymerization process. The total charges of all synthesized polymer films were in the range between 5 and 12 mC/cm^2, thus suggesting very thin films.

Freshly synthesized films were transferred into electrolytic cell with monomer free solution of 0.1M $LiClO_4$ in acetonitrile, and kept at the potential E_p = 0.6 V in order to erase the electrochemical history of the samples. The transition from E_p to the wait potential E_w was direct. The relaxation behavior was followed during different wait times in the range between 10 and 5200 seconds. The first CV cycles were analyzed after the samples were maintained at potential E_w = -200 mV.

All electrochemical measurements were performed with HEKA potentiostat-galvanostat type 488 interfaced with personal computer.

Results and discussion

The doping process in the electrochemical preparations of polymer films proceeds by simultaneous insertion and penetration of dopand anions from the working electrolyte which promote movement of the macromolecule chains [8]. Their presence induces reorganization of polymer chains into thermodynamically unstable states, far away from the equilibrium state. The reduction process, followed by expulsion of anions, should be the process which returns the system into equilibrium. But not all dopand anions are capable of leaving the polymer matrix during the potential scan in cathodic direction. To achieve complete reduction, it is necessary to maintain the polymer film for some time in neutral state, in order to expel the remaining dopand anions and thermodynamically stabilize the system. This conversion is a very slow process, which is followed during the wait time t_w.

The characteristic *I(E)* profiles, obtained after different wait times for poly(3-methyl thiophene) and poly(3-octyl thiophene), are presented in Figures la and lb. Similar *I(E)* profiles are registered for poly(thiophene). It could be noted that the peak potentials and currents of the relaxed waves are shifted to more positive values, compared to the so-called “steady state” peak, obtained by continuous cycling. By increasing the wait time, relaxed peaks become sharper, as shown by the lower width of the peak at half current $\Delta E_{1/2}$.

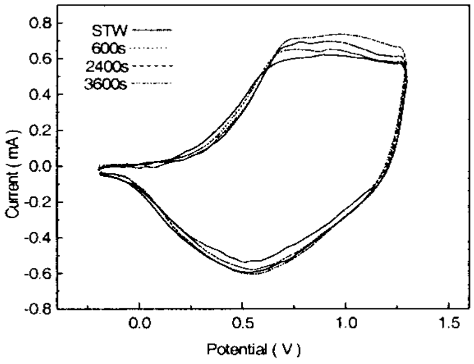

Figure 1a. I(E) profiles of poly(methyl thiophene) film deposited onto Pt electrode obtained after different wait times

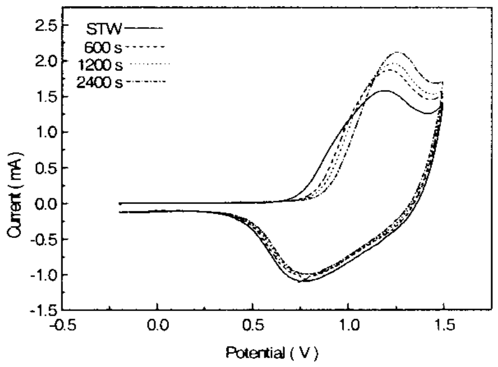

Figure 1b. I(E) profiles of poly(octyl thiophene) film deposited onto Pt electrode obtained after different wait times

The last peak parameter has decreasing character for all investigated homopolymers (Figure 2), and associates with the left half of the peak, due to its asymmetry and considerable influence of the capacitative current. It could be observed that $\Delta E_{1/2}$ at poly(octyl thiophene) varies significantly in comparison with PMT in the same range of wait times. $\Delta E_{1/2}$ does not depend linearly on the logarithm of the wait time as has been reported in literature [9].

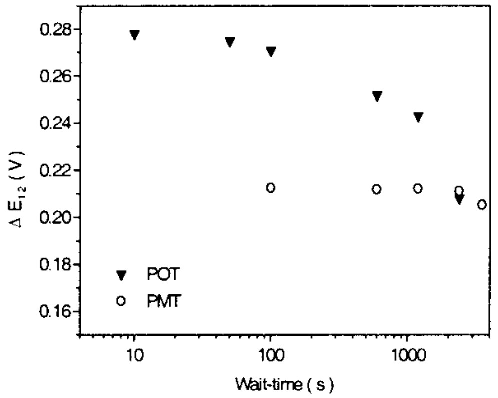

Figure 2. $\Delta E_{1/2}$ left half, dependence on the logarithm of the wait time at PMT and POT films grafted on Pt electrodes

The changes of the potential and current with the logarithm of wait time, given with the equations 1 and 2 (reported elsewhere [5]) are presented in Figures 3a and 3b for all the investigated homopolymers.

$$E(\tau)= E_o + \delta_{e\tau} \log \tau \tag{1}$$

$$I(\tau)= I_o + \delta_{i\tau} \log \tau \tag{2}$$

where I_o and E_o are constants, and $\delta_{e\tau}$ and $\delta_{i\tau}$ are slopes of the presented relations. Linear correlations have been obtained for wait times greater than 100 s.

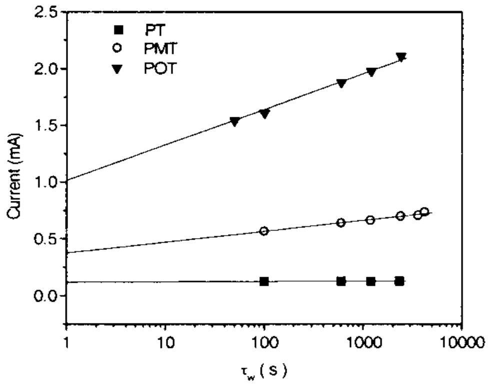

Figure 3a. Semi logarithmic plot of I_p vs. t_w for PT, PMT and POT films deposited onto Pt electrode

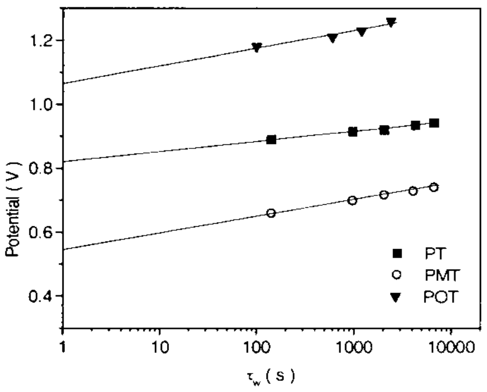

Figure 3b. Semi logarithmic plot of E_p vs. t_w for PT, PMT and POT films deposited onto Pt electrode

Different slopes are obtained by linear fitting of the presented relations. The slopes derived from the potential equation are 15.8, 44.8 and 55.2 mV/decade, while those derived from the current relation are 0.0031, 0.096 and 0.35 mA/ decade for PT, PMT and POT respectively. The slopes as characteristic parameters of relaxation could give a clear picture for the kinetics of doping process at these polymers. It could be concluded that the slopes increase with increasing the length of the alkyl substituent. In the further discussion we will discuss the slope $\delta_{e\tau}$ as it is known that the potential is more sensitive to the progressive alteration of the polymer film properties during the course of the experiment than the peak height.

According to this the relaxation process i.e. the kinetics of doping should be directly connected with the polymer structure and therefore with its morphology since it is well known that the alkyl substituent has considerable influence on the morphology [10]. Homopolymers with shorter side segments form more compact films similar to poly(thiophene), while those with longer side groups like poly(octyl thiophene) are characterized with less regular structure and considerably porous films. The main reason for such a behavior is the fact that the longer substituents increase the distance between the main conjugated chains. Following this, the mobility of the side substituents is higher, as a result of the more space left around the main conjugated segments. In that case the dopand anions are easily accommodated between the chains and easily move in and out of the polymer matrix. Therefore, the changes in the polymer film morphology have significant influence on the doping-dedoping processes.

Similar behavior, even though it is a different phenomenon, could be observed at the thermal undoping process, described by several authors [11, 12]. Granstrom et al. have shown that the process of thermal undoping is faster in poly(octyl thiophene) than in poly(butyl thiophene) due to the higher mobility of the octyl side chains [13]. On the other hand, such a behavior is usually a cause for some unwanted effects, like polymer system instability in the doped state, because of the easy kicking out of dopand anions from the polymer matrix. In this context the possible interactions between the alkyl chains that could also have great influence on the relaxation process will not be discussed.

The investigated films were also electrodeposited onto Ti electrodes (with an exception of PT), in order to study the influence of the electrode material on the kinetics of relaxation behavior of the polymers. The *I(E)* curves for PMT and POT deposited onto Ti electrodes are presented in Figure 4a and 4b.

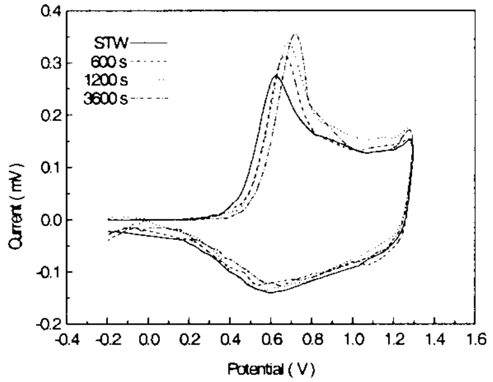

Figure 4a. I(E) curves for PMT film deposited onto Ti electrode

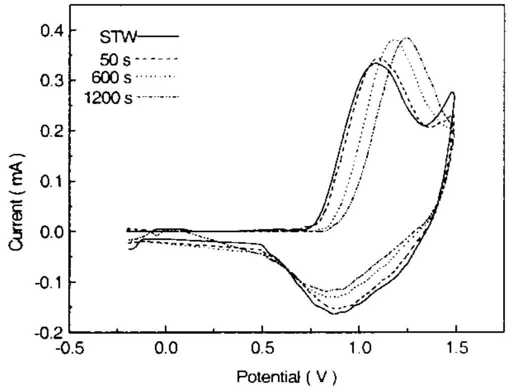

Figure 4b. I(E) curves for POT film deposited onto Ti electrode

By comparing the last *I(E)* profiles with those characteristic for the same polymers deposited on platinum, considerable shifting of the relaxed peaks could be noted at poly(octyl thiophene) grafted on titanium electrode. It could be confirmed by the slope $\delta_{e\tau}$ which increases double (106 mV/decade) in comparison with the $\delta_{e\tau}$ received for POT deposited onto platinum electrode (Figure 5).

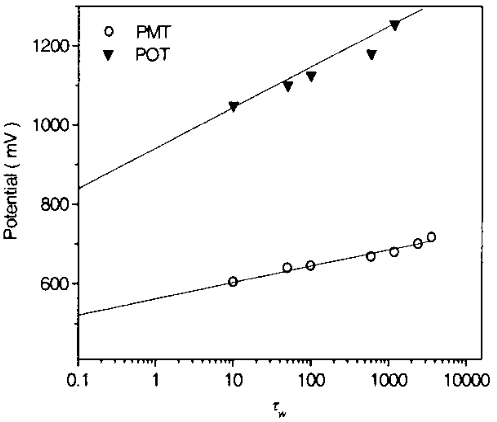

Figure 5. Semi logarithmic plot of E_p vs. t_w for PMT and POT films deposited onto Ti electrodes

The slope $\delta_{e\tau}$ at PMT does not change either, has value of 42 mV/decade and is approximately the same as the slope at PMT grafted on Pt electrode ($\delta_{e\tau}$=44mV/decade).

From the kinetic point of view, it could be considered that the relaxation process at the samples with longer alkyl chains and deposited onto Ti is faster compared to the samples with shorter alkyl segments, electrodeposited onto Pt electrode. The main reason for such a behavior could be ascribed to the nature of the electrode material. The substrate is considered as integral part of the electrochemical process [14].

Namely, the nature of the substrate dictates the orientation of the monomer unit, and therefore the orientation of the polymer chain with respect to its surface. Such a dictated orientation probably causes the changes in the polymer film morphology.

Bazzaoui et al have illustrated the influence on the substrate on the thiophene rings orientation by comparing platinum and silver electrodes [15]. Tourillon at al. have also shown that poly(methyl thiophene) chains lay flat onto metal surface, while the polymers with longer chains are perpendicular to the substrate [16].

From this point it is evident that the polymer chains orientation i.e. the angle between the chain and the metal surface has great influence on the kinetics of doping–dedoping processes.

Conclusions

Our measurements suggest that the kinetics of the relaxation process depends on the structure of the polymer film and the nature of the metal substrate. The relaxation process is faster at polymers with longer alkyl substituents deposited onto titanium surface.

The rate of relaxation process in poly(methyl thiophene) does not depend on the nature of the electrode material since poly(methyl thiophene) chains probably lay flat onto the substrate surface, causing no significant changes in the polymer film morphology.

The longer alkyl substituents are the main reason for larger space between the main conjugated chains, resulting in their higher mobility and more space left to accommodate dopand anions, therefore resulting in faster relaxation process.

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