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Time-Resolved Study of the Mechanism of Photogeneration of Free Charge Carrier in Semiconducting Polymers

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The problem of distinguishing the photocurrent caused by the drift of free polarons from that produced by polarisation of neutral excited species is discussed. New pump-and-probe technique with monitoring the average photoconductivity changes permits to overcome these difficulties when studying primary processes of free charge carrier photogeneration. Models of those processes are considered in conditions of fs UV-light pulse excitation of polymeric samples, and probing intermediate excited species by the photocurrent changes caused by delayed red pulses. Negative changes are indicative for the role of intermediate excited species like excitons and polaron pairs. Second order processes between polaron pairs seem to play a role in free polaron formation at high excitation rate.

Keywords: organic semiconductors; charge carriers; polaron pairs; excitons; photoconductivity; time-resolved fast spectroscopy

INTRODUCTION

Electronically excited states are formed as a rule at photoexcitation of molecular solids within the main absorption band. Following events resulting in appearance of free charge carriers are autoionization of

excited states; their relaxation down to excitonic states; reactions of excitons with impurities and ionization of the latter; and so on. However, two different approaches are used for description of photoelectric properties of polymers with a system of conjugated double bonds. The first one is based on the model mentioned above. Another model assumes the absorption of the light to occur at band-to-band electron transition similar to that taking place in inorganic semiconductors. Free charge carriers are generated in the primary process according to the second model. Papers [1-3] and the book [4] are devoted to comparison of the two approaches, which coexist so far. An experimental approach to the problem of choosing the right model consists in studying a transient photoconductivity within the time domain of lifetimes of electron excited states. A few papers were published up to date having been devoted to investigation of transient photoconductivity induced in conducting polymers by pico- or femtosecond laser pulses (in polyacetylene [5,6], polydiacetylene [5, 7], polyphenylenevinylene [8-10]). A prompt component of transient photoconductivity with the lifetime in 10 ps range was seen in all cases, its properties having been very interesting. It appeared during the exciting pulse, increased linearly with the intensity of the exciting light, and its amplitude and the decay rate did not depend on the temperature. That component was speculated to be a manifestation of primarily formed free charge carriers [9, 10]. However, all possible reasons of appearance of prompt component were not analyzed in the papers [5-10]. It prevents from coming to any definite conclusion about the validity of the models of the light absorption and subsequent processes. Indeed, electron excited molecules are among the polarizable species formed under photoexcitation. For polymer molecules with a system of conjugated bonds its magnitude is of an order of $\alpha \approx 10^{-21} - 10^{-20}$ cm^3

[11]. Deformation and shift of an electron cloud proceeds under the action of electric field extremely fast ($\tau_{pol} \approx 10^{-15}$ - 10^{-14} s), and conserves during the lifetime τ_{exc} of excitation within the polarizing electric field. Highly polarizable are species of another nature formed by two charged particles like charge-transfer excitons and polaron pairs. They decay in the first order processes (geminately), and are precursors of free charge carriers according to excitonic model of photoconductivity. Their polarizability can be as high as $\alpha \approx 10^{-19}\text{cm}^3$ [12]. The decay of polarized species is accompanied by the distraction of the polarization produced, which looks like the displacement current but of the opposite direction. Total charge transfer in the circuit equals to zero. Kinetics of the displacement current can be described by the next formula [12]

$$i_p = N_{pol}\alpha\frac{V}{l^2\tau_{pol}}\left(e^{-\frac{t}{\tau_{pol}}} - \frac{\tau_{pol}}{\tau_{exc}}e^{-\frac{t}{\tau_{exc}}}\right) \qquad (1)$$

Here N_{pol} is an amount of polarizable species formed in the sample, l is the distance between electrodes.

Figure 1 demonstrates this dependence. It is worth noting that as far as $\tau_{exc} >> \tau_{pol}$, the depolarization current is invisible on the scale of the positive polarization current. Thus, straightforward measurement of transient photocurrent does not permit to be sure that it is connected with free charge carriers.

MODIFICATION OF THE PUMP-AND-PROBE TECHNIQUE

Another approach for studying the primary events is provided by the well-known pump-and-probe technique. It permits to get knowledge on

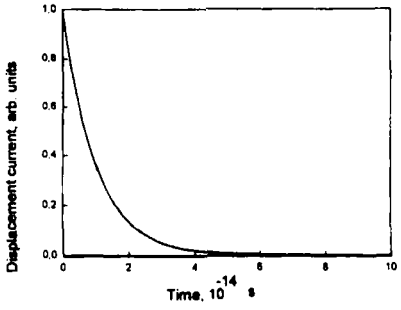

FIGURE 1. Kinetics of the displacement current $i_p(t)$ caused by polarization and decay of neutral excited states formed instantaneously at $t = 0$. Parameters $\tau_{pol} = 10^{-14}$ s, $\tau_{exc} = 10^{-9}$ s.

the formation of short-lived intermediate species, but gives no hints whether they are charged or not or are they arranged in pairs or not. In order to be able to deal with free charge carriers one has to study cw photocurrent. Does it mean one has to forget the time-resolution? We believe that a modified pump-and probe technique is able to unite both features. Modification consists in monitoring changes in average photoconductivity induced by the probing (red) pulses whereas the pump (blue) pulses acting within the main absorption band produced all the excited species. First attempt to apply that modified technique for semiconducting polymers was published in [13]. Experiments on substituted poly(3-alkyl-thiophene) (P3AT) and poly(phenylene vinylene) (OO-PPV) films were performed by direct probing the formation of charge carriers responsible for the photoconductivity within the time domain from 1 ps to 1 ns. Laser light pulses of 400 nm wavelength, 150 fs width, induced photoconductivity in a sample. Red 800 nm light pulses delayed in respect to blue ones were revealed to affect the photoconductivity. Effect of the second pulses was zero at

zero delay time and increased later on as it is shown in the Figure 2. Fitting (solid curve) shows 15 ps and 150 ps delayed components corresponding to lifetimes of free polaron precursors.

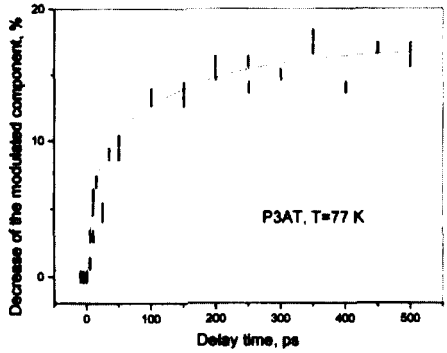

FIGURE 2. Changes of the photocurrent caused by the red pulses as a function of the delay time between blue and red pulse [13].

Red light induced changes of a hopping mobility of polarons, according to the model suggested. These results were rationalised as an evidence of delayed not immediate formation of charge carriers belonging to polaron pairs, in contrast to what could be expected from the band-to-band model of photoconductivity.

Here we consider a scenario of processes that could take place under conditions of correlated laser pulse excitation of a sample, and possible connection of the photoconductivity changes with rate constants governing the behavior of intermediate excited species involved.

POLARON PAIR MODEL

Blue pulses of the laser light provide the excitations of a high density. Typical pulse energy is within μJ range corresponding to quantum absorption rate of the order of 10^{18} quantum/cm^3 per pulse. We assume that polaron pairs are generated (directly or by electron transfer from molecular excitons) in two steps. The first one contains primary polaron pairs P_1 with more mobile charge carriers (mobility μ_1). After fast relaxation they become thermalized polaron pairs P_2 with carrier's mobility μ_2. Next kinetic equations describe the behavior of the pairs

$$\frac{dP_1}{dt} = g(t) - \frac{P_1}{\tau_1} - k_{loc}P_1 - k_1P_1P_2 \qquad \text{at } t=0 \quad P_1=P_{10} \tag{2}$$

$$\frac{dP_2}{dt} = k_{loc}P_1 - \frac{P_2}{\tau_2^*} - k_{th}^*P_2 - k_1P_1P_2 - k_2^*P_2^2 \qquad \text{at } t=0 \quad P_2=0 \tag{3}$$

Here $g(t)$ is the rate of formation of polaron pairs; P_1 and P_2 are densities of primary and thermalized polaron pairs, respectively; τ_1 and τ_2 are their lifetimes in respect to geminate recombination; k_1 and k_2 are rate constants for random recombination (interpair recombination); k_{th} is the rate constant for dissociation of polaron pairs and formation of free polarons. Asterisks mark the parameters subjected to alternation under the action of the red light pulses.

Interpair random recombination terms in Eqs. (2) and (3) may be considered as those responsible for the appearance of free charge carriers: recombination of two charges from different pairs leaves two other charges at higher intercharge distance and gives them a chance to get free. Next kinetic equation works for free polarons:

$$\frac{dp}{dt} = \alpha(k_1 P_1 P_2 + k_2^{\bullet} P_2^2) + k_{th}^{\bullet} P_2 - k_2^{\bullet} p^2 \quad \text{at } t = 0 \quad p = 0 \qquad (4)$$

Here $\alpha<1$ is the yield of free charge carriers formed per one interpair recombination event. Solution of the system of equations (2) to (4) and averaging of p over regularly repeated excitation pulses permits describing the photocurrent generated by the sequence of blue pulses. The role of red pulses consists in changing the values of rate constants related to the increased mobility μ_2 of charge carriers: k_2 and k_{th} increase, τ_2 decreases, though these changes being initiated by the action of the red pulse can last for about 10 ps (lifetime of pretrapped polarons) only. It follows from Eqs. (2) to (4) that photocurrent contains the component connected with drift of pretrapped carriers p_1 that escaped geminate recombination. The drift occurs with red-light-independent mobility μ_1

$$p_1 = \alpha \frac{k_1 P_{10}^2}{\left(\frac{1}{\tau_1} + \frac{1}{\tau_2} + k_{loc}\right)}; \qquad \frac{\Delta p_1}{p_1} = \frac{\Delta \tau_2}{\tau_2^2 \left(\frac{1}{\tau_1} + \frac{1}{\tau_2} + k_{loc}\right)} \qquad (5)$$

One can see that red light induced changes Δp_1 of this component are negative as far as the lifetime τ_2 of a polaron pair decreases on $\Delta\tau_2$ under the action of a red pulse. There is one more component of the photocurrent caused by drift of thermalized polarons with the mobility μ_2. The term $k_{th}P_2$ is another source of free charge carriers as well. It becomes more abundant under the action of red light, and is responsible for the positive changes of the photocurrent. Relative magnitude of the positive and negative changes depends on the density of polaron pairs P_1. For higher density negative changes are expected to prevail. In experiments made [13] both negative and positive changes were

observed. Figure 2 shows a plot obtained for poly(alkyl thiophene) (P3AT) sample. The changes are negative here.

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