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Fullerene Doping and External Electric Field Effects of Second Order Processes of Photoconductivity in Poly(3-alkylthiophene) Utilizing Femtosecond Pulse Laser Technique

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Photogeneration and recombination of free charge carriers are the processes, which are involved many applications of conducting polymers. That is why studying their mechanism was considered to be very important. Many works were devoted to investigation of processes responsible for appearance of charged species under photo excitation [1]. Most of them came to the conclusion that charge carriers appear immediately as a result of the light absorption, though it remains uncertain whether the corresponding process can be described as band-to-band transition, or as a fast electron-transfer process from primarily generated intra-chain excitons. In conducting polymers, dependence of amplitude of photoconductivity by the light excitation was linear process at low excitation intensity, but became second order process at high excitation intensity. The polaron pairs have shown themselves in the second order processes that were the main supplier of free charge carriers at high excitation density. But, we would like to claim that pump-and-prove technique currently used by present is not fulfills the sufficient conditions for their free carrier formation in the of second order processes. In a general way, the mobility of conducting polymers is much smaller than that of inorganic semiconductors. Because of the low mobility in of conducting polymers,the positive and negative charge carriers of polaron pairs in Onsager's radius recombine geminately. Consequently, zero net shift contribution occurs to the cw conductivity. That is a sequence of very fast energy loss by the charge carriers that is reflected in their low mobility values. These polaron pairs must be free to drift under the action of an electric field, and be shifted by the field during their lifetime [2,3]. A small part of the pairs manages to dissociate and contribute to conductivity. In order to get a direct existence of the second order processes of photoconductivity, we measured the photocurrent during the time interval longer than the lifetime of the pairs utilizing two-correlated-pulse technique. Two-correlated-pulse technique can permit to resolve kinetics of the free charge carrier formation within the picosecond time domain [4].

Dissociation of the pairs does not appear to be the only way of free charge carriers for-

mation, but can be formed also as a result of inter-pair recombination [4,5]: two charges from neighbour pairs recombine just leaving two remaining charges at longer inter-charge distance and thus increasing their chance to be outside Onsager's radius and to be free polarons.

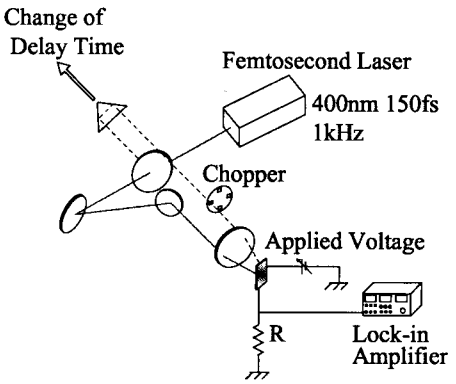

Fig. 1: Scheme of two-pulse-correlation technique.

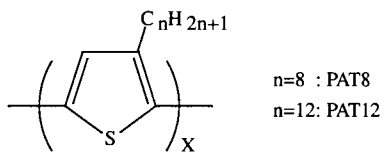

Fig. 2: Structure of PAT in this study.

In such a background, we have been carriying out the investigation as follows: (1) the first was the measurement of photocurrent under this technique versus the electrical field strength, which permit to find out the changes of the free carrier yield connected with the dissociation of the pairs. (2) Quenching of the photoluminescence and increasing of the photocurrent by doping of fullerene into PAT was known in our previous results [7]. The question is whether the charge carrier formed as a result of the charge-transfer between conjugated segments and acceptor molecules are arranged in pairs that can do inter-pair recombination, or they dissociate becoming free immediately after their appearance? In this study, we studied fullerene (C_{60}) doping and external electric field effects of the first and second order processes responsible for the formation of free polarons in poly(3-octylthiophene) (PAT8) and poly(3-dodecylthiophene) (PAT12) under the two-correlated-pulse laser light excitation as shown in Fig.1.

The wavelength and pulse width of the two-correlated-pulse laser were 400nm and 150fs, respectively, and were controlled the delay time between two pulses. There were a feature in the action, which change the yield of the second order processes as a function of the delay time under the condition of the constant average intensity in the laser excitation. Thin polymer films were prepared by casting method from the toluene solution of the polymers onto interdigital Au electrode substrate, the interval of electrodes of which was 5μm. All measurements were carried out in vacuum by putting the sample into a cryostat at room temperature. Free charge carrier formations of the first and second order processes involved the primary formation of pretrapped polaron pairs, thermalization of the pairs, dissociation and inter-pair recombination [6].

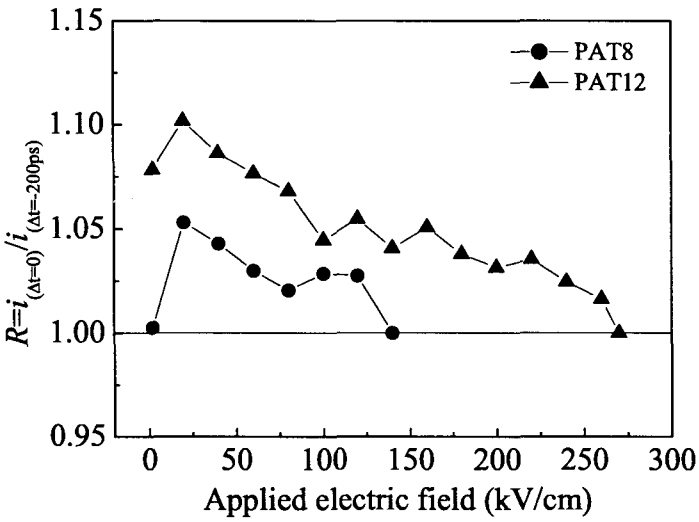

Fig. 3: Dependence of the ratio R on the electric field strength.

Figure 2 shows a molecular structure of PAT8 and PAT12 used in this study. This synthetic method is already reported. In our experiment, typical transient photocurrent of the second order processes with the applied electric field strength which was from 2×10^3 to 3×10^5 (V/cm) at delay time $\Delta t=0$ was detected and the half-width of photocurrent of maximum intensity was about 5ps in these polymers. It was considered that lifetime of polaron pairs for the second order process could be estimated to be about 5ps. The electric field strength dependence of modulated photocurrent ratio R of $\Delta t=0$ and Δt=-200 (ps), $R=i_{(\Delta t=0)}/i_{(\Delta t=-200)}$, is exhibitted in Fig.3 about PAT with different side chain length. Maximum value of R could be detected around 20 (kV/cm) in both case of PAT8 and PAT12. But, with increasing applied electric field strength, the photocurrent ratio R was decreased. The ratio R of PAT12 is larger than that of PAT8. Because of long side chain length in PAT12 has a character that the distance between the main chains is large and is easy to confine exciton polarons, it is considered that nonlinear photocurrent is large.

Figure 4 shows fullerene doping effects of photocurrent in the second order process with changing the delay time. Doping concentrations were 0, 0.1, 0.3 and 0.5 mol%, respectively. When the fullerene doping concentration was increased, the linear component of photocurrent was enhanced, but the nonlinear component of photocurrent at $\Delta t=0$ decreased relatively. Since fullerene originally has the function as an acceptor, Most of the free polarons' formation should be due to the photoinduced charge transfer between PATs and C_{60}. This is considered to be the reason why the free polarons for nonlinear current were not enhanced.

In conclusion, we measured photocurrent of the second order processes with changing the delay time between two excitation pulses, the wavelength and pulse width of which were

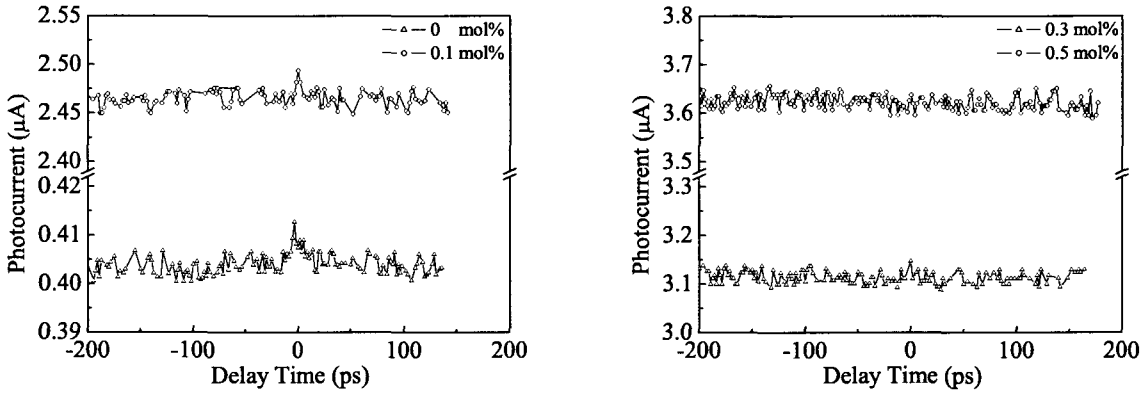

Fig. 4: Fullerene doping effect of photocurrent with changing the delay time. Concentration of fullerene are 0, 0.1, 0.3 and 0.5 mol% repectively.

400nm and 150fs respectively in poly(3-alkylthiophene) (PAT) with different side chain length. These polymers are shown to take part in the second order processes in the free carrier formation contributed to the photocurrent. Applied electric field strength or fullerene doping to PAT leads to decrease of the ratio R.

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