On properties of polymeric semiconductors having a critical effect on the photovoltaics

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Organic semiconducting polymers are similar to molecular crystals as both of these materials have weak van der Waals bonding between the molecules, and individual conjugated segments absorb light as separate molecules do. Segments of conjugated double bonds can provide free paths for excess charge carriers along all their length (up to 4 nm usually), though the average mobility of the carriers remains low and is limited by the rate of hops between the segments. Typically it has the value $\mu = 10^{-6}$ to 10^{-4} cm^2/V s. According to present state of knowledge the photoexcitation of conjugated polymers generates intrachain singlet excitons. Radiative decay of the excitons results in fluorescence (for poly(*p*-phenylene vinylene) (PPV) 0-0-transition being localized at 2.37 eV. Alternatively, primary singlet excitations can produce triplet intra-chain excitons by intersystem crossing, or transfer an electron to the neighboring chain or to the next conjugated segment of the same chain. These processes form charge-transfer (CT) inter-chain excitons, or polaron pairs. From next-neighboring-chain sites, movable polarons can hop to further chain sites still belonging to the pair. Thus, only a small part of primarily formed pairs of charges has a chance to escape from geminate recombination and become free charge carriers. In order to do that a charge carrier inside the Coulomb well must overcome a potential barrier ΔU_0, which depends on the separation distance r between charges in the pair: $\Delta U_0 = e^2/\varepsilon r$.
Quantum yield of free charge carriers β is proportional to $exp(-\Delta U_0/kT)$, and for intrinsic charge carrier generation it is very small, usually about $\beta = 10^{-3}$. External electric field is able to increase β significantly since the field decreases the barrier, subtracting from ΔU_0 an amount of about rEe, where E is the electrical field strength.

Sensitization of the photoconductivity of conjugated polymers by doping. Polaron pairs formed in a semiconducting polymer with similar conjugated segments have only small probability of dissociation into free polarons. But it was discovered by Osaka and Santa Barbara groups, independently that the yield of free charge carriers can be highly increased by doping of the polymer by electron acceptor molecules. Addition of C_{60} molecules to PPV was revealed to lead to quenching of the fluorescence of the polymer and to appearance of high photoconductivity. Increase of the photoconductivity can be achieved by adding to a polymer other molecular acceptors and even molecular oxygen though photochemical reactions with O_2 destroy the material soon. These facts may be described as super fast formation of pairs of the $(D^+ A^-)$-type, which have a high rate of dissociation and small rate of recombination. Physical reason for that is a reduction of the barrier for dissociation of polaron pairs on the value equal to electron affinity of the dopant molecule: $\Delta U \approx \Delta U_0 - EA(A)$
Electrical field can help to the dissociation additionally, and as a result quantum yield of free carrier generation β can reach the value close to unity. Thus, one can hope that the problem with a proper value of the quantum yield can be solved for semiconducting polymers. The price for the higher quantum yield is a loss in the energy available for conversion into electrical one since the energy released at the electron-transfer process (equal to electron affinity of dopant molecule) goes into heat.

On the importance of a high mobility value. One has to notice that sensitization of free carrier photogeneration by doping leads to formation of electrons localized on acceptor molecules. But for many applications of photosemiconductors, and particularly for photovoltaic, it is important to have the charge carriers mobile and able to reach the electrodes. To overcome this difficulty one can use higher concentration of dopants in order to permit electrons to jump between molecules A, or to use two-layer system, polymer and dopant layers, generating charge carriers on interface and permitting to positive and negative polarons to travel in different layers. Nevertheless low value of charge carrier mobility remains a narrow site in many applications of semiconducting polymers.

Competition of bulk recombination of charge carriers and their drift to electrodes. Charge carriers generated by the light absorbed within the active layer of the photovoltaic cell must have high enough probability to reach electrodes. Efficiency of the light-to-electricity conversion directly depends on that probability. However, one of the most important competing factors is bimolecular recombination of charge carriers. Recombination is relatively faster than drift between electrodes at low mobility of charge carriers.

We estimated the charge collection efficiency C as a ratio of amount of carriers that is reaching the electrodes in a sandwich sample to the amount of primarily generated free charge carriers gl (per 1 cm^2) : $C = i/gl$, where $I = \mu Vn/l$, and l is the thickness of a polymer layer between electrodes. Collection efficiency C, i.e. a part of photogenerated charge carriers that escapes recombination and reaches electrodes, is given by the next formula (for steady-state illumination)

$$C = \frac{\mu^2 V^2}{2\gamma l^4 g}\left(\sqrt{1+\frac{4\gamma l^4 g}{\mu^2 V^2}} - 1\right).$$

This formula permits to estimate the mobility required for achievement high enough collection efficiency, if the universal connection of μ and recombination rate constant γ is used: $\gamma = \frac{4\pi e\mu}{\varepsilon}$. Thus, for typical values of parameters of polymeric solar cell, $V = 1$ V, $l = 0.1$ μm (high light absorbance is needed for that value of l), dielectric constant $\varepsilon = 4$ and $g = 2.5\mathrm{x}10^{22}$ (at solar light intensity 100 $\mathrm{mW/cm}^2$ and extinction $\varepsilon = 10^5\ \mathrm{cm}^{-1}$) $C = 0.9$ at $\mu = 10^{-3}\ \mathrm{cm}^2/\mathrm{Vs}$; but $C = 0.3$ at $\mu = 10^{-5}\ \mathrm{cm}^2/\mathrm{Vs}$. The results are presented in Figs. 1 and 2. They show that the lower is the mobility the relatively higher is the recombination rate, and the collection efficiency decreases. Thus, effective work of photovoltaic solar cells requires charge carrier mobility to be not lower than $\mu = 10^{-3}\ \mathrm{cm}^2/\mathrm{Vs}$. Even higher value of μ is needed for thicker than $l = 0.1$ μm polymer film. Thus, for $l = 0.2$ μm $\mu = 10^{-2}\mathrm{cm}^2/\mathrm{Vs}$ is needed. Is it possible to work effectively with the material with low charge carrier mobility? Let us discuss this question.

Summary. Next properties of polymeric semiconductors as a material for light-to-electricity converters are most important for effective work:

1. High light absorbance within the solar light spectrum ($\varepsilon = 10^5\ \mathrm{cm}^{-1}$). It will permit to work with thin polymeric layer.
2. Choosing proper pairs of donors and acceptors, both polymeric and other, to ensure a high quantum yield of free charge carriers. Care has to be taken for the possibility of free drift of positive and negative charge carriers generated in charge-transfer processes.
3. Preparation of polymer films with regular positions of conjugated segments and acceptor dopants for higher mobility of charge carriers (not lower than $\mu = 10^{-3}\ \mathrm{cm}^2/\mathrm{V\ s}$).

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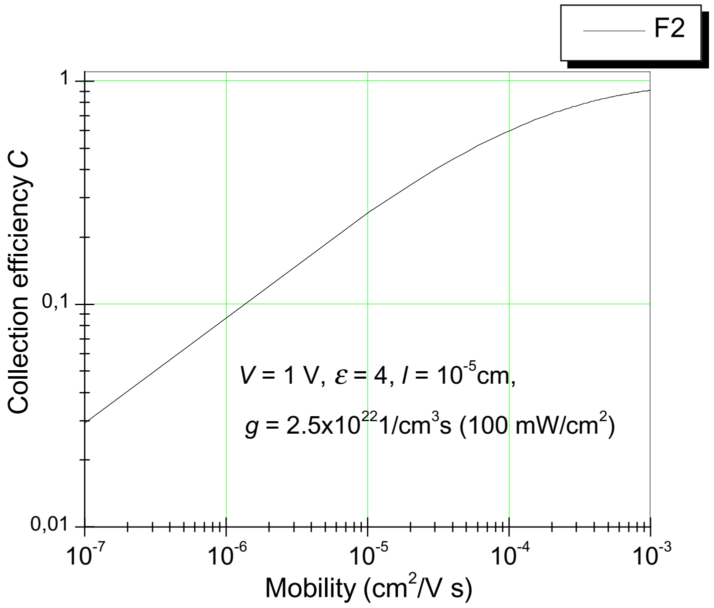

Figure 1

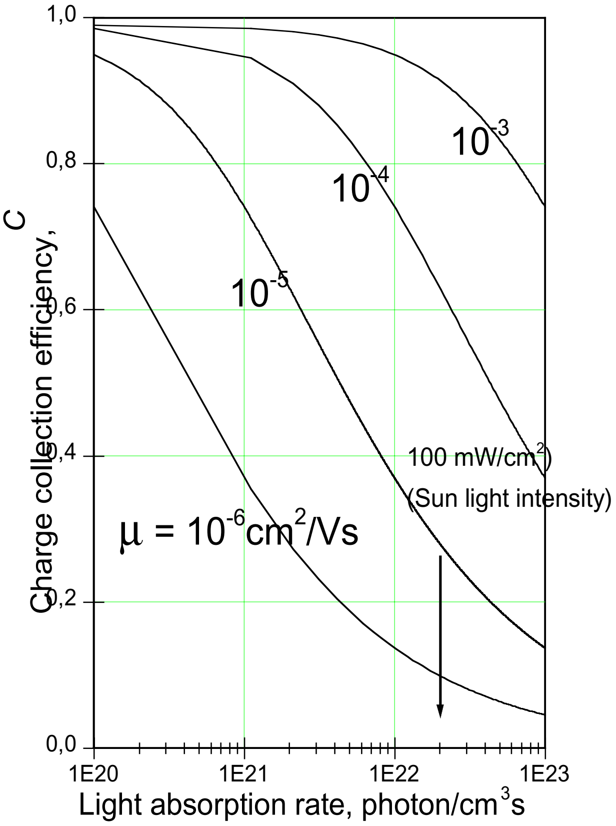

Figure 2.