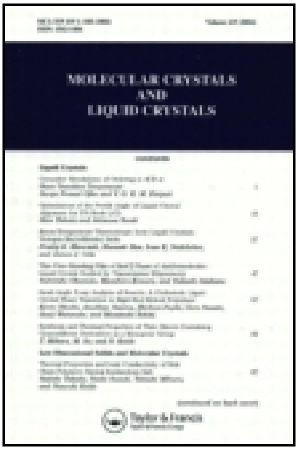

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Molecular aggregate formation and microphase segregation effects on the photoelectrical and photovoltaic properties of polyimide-perylenediimide composite films

B. M. Rumyantsev [a] , V. I. Berendyaev [a] , A. Yu. Tsegel'skaya [a] & B. V. Kotov [a]

[a] "Karpov Institute of Physical Chemistry", State Science Center, 10 Vorontsovo pole str., Moscow, 105064, Russia

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MOLECULAR AGGREGATE FORMATION AND MICROPHASE SEGREGATION EFFECTS ON THE PHOTOELECTRICAL AND PHOTOVOLTAIC PROPERTIES OF POLYIMIDE-PERYLENEDIIMIDE COMPOSITE FILMS

B. M. Rumyantsev, V. I. Berendyaev,
A. Yu. Tsegel'skaya and B. V. Kotov
State Science Center "Karpov Institute of Physical Chemistry",
10 Vorontsovo pole str., Moscow 105064, Russia

The strong increase of electrophotographic sensitivity, charge carrier photogeneration quantum yield and improved photovoltaic characteristics (sandwich cells with ITO, Al electrodes) are found for films of photoconductive soluble polyimides based on doubled triphenylamine heavily doped by the soluble perylenediimides (with content up to 50–60% wt). It is shown that the effect is due to perylenediimide aggregates of some tens nanometers size which are formed during the film casting at high solvent evaporation rate. The further increase of photoelectric and photovoltaic parameters is achieved by using the films of polymer blends of polyimides with polyetherimides (Ultem-1000 type) also doped with soluble perylenediimides. In this case the effect is due to microphase segregation in doped polymer blend films caused by the partial incompatibility of polymers, that results in the formation of microregions with n- and p-types of photoconductivity contacting with each other and possible appearance of p-n bulk microheterojunctions.

Keywords: polyimides; perylenediimides; composite; electrophotographic sensitivity; charge carrier photogeneration; aggregates; polyetherimide; microsegregation; photovoltaic cell

Among the various applications of photoconductive polymer electron donor-acceptor systems, in particular polyimides (PI), one of the perspective is the application for photovoltaic solar cells [1,2]. In this work the progress in improvement of the photoelectrical and photovoltaic (PV) characteristics of cells based on films of doped high sensitive soluble PIs with doubled triphenylamine chain donor groups is demonstrated [3,4].

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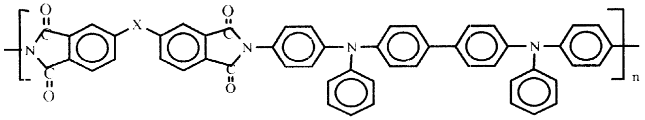
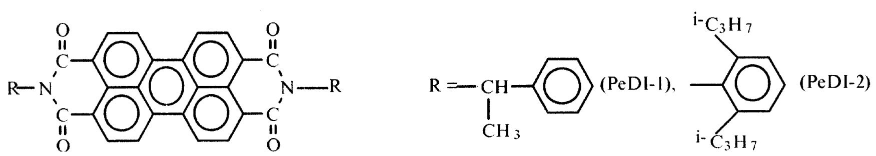


X = O (I), —(II), CO (III)

The interest in this field is stimulated by the fact of very high radiation, photochemical and temperature stability and excellent filmforming properties of PIs.

It has been shown earlier that films of these PIs sensitized with dyes as well as some fullerene derivatives display high charge carrier photogeneration quantum yield and PV effect under visible light excitation in sandwich cells with ITO and vacuum evaporated Al electrodes [2,5]. But the overall energetic conversion efficiency of these PV cells is rather low (about 0.01%) because of low electron mobility in triphenylamine containing PI films which are presumably hole photoconductors [6] and as a result high carrier bulk recombination rate. One of the methods to prevent the effective bulk recombination consists in using the microsegregated polymer blends and compositions in which electron donor and acceptor components form separated phases with large interface area between them [7].

In this work the strong increase of charge carrier photogeneration quantum yield (β), electrophotographic sensitivity (S_λ) and essential improvement of PV characteristics are found for films of PI and its blends with polyetherimides doped by soluble perylenediimides (PDI) as electron acceptors (EA = 1.8–2.0 ev) of structure at content from 0.5 to 50–60% wt.



The films were prepared by casting of combined solution onto preheated ITO glass substrates with the next drying for five hours at 100°C in the air. The film thickness for electrophotographic measurements was 2–3 μ and for PV cells – 0.5–1.0 μ. It was found that high solvent evaporation rate results in the formation of visible homogeneously coloured films containing PDI aggregates which presence could be concluded from optical microscopic observations, decrement of extinction coefficient in PDI absorption band for solid films, PDI luminescence quenching and intensive light scattering. There were the aggregates of various sizes inside the film distributed from 0.1–0.5 μ to molecular ones. In addition there were also PDI isolated molecules.

It is found that increase of the electrophotographic sensitivity upon PDI concentration rising in films of various PIs is due to β concentration increment for high PDI content ($C \geq 10\%$ wt) while for low $C < 10\%$ wt – due to increase of absorbed light fraction in PDI longwave band until its value overcome 90% (Fig. 1).

The highest S_λ and β values are obtained for PIs doped by PDI-1 which shows lower solubility as compared with PDI-2 at high solvent evaporation rate. For more soluble PDI-2 the highest S_λ value is much lower and it is achieved at low solvent evaporation rate. Since it is the balance between solvent evaporation and PDI crystallization rate depending on PDI solubility that determines the aggregate size these facts imply that the formation of PDI aggregates of definite optimal size is the crucial moment for the appearance of high sensitivity.

This conclusion is confirmed by the strong electric field dependence of β (E) for various PDI contents in PI films (Fig. 2). As it is well established the β value field dependence indicates the Coulombic bounded electron-hole pair formation which field assisted thermal dissociation results in the free charge carrier generation. The interpretation of β(E) dependences (Fig. 2, curves 1–4) in accordance with Onsager model of pair geminate

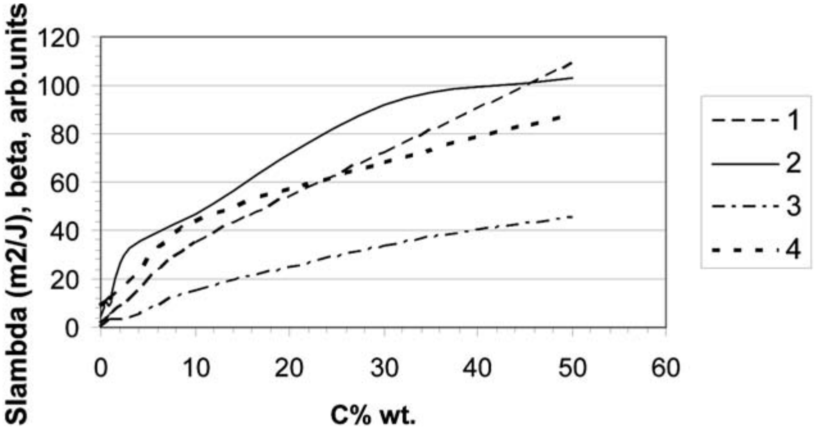


FIGURE 1 Electrophotographic sensitivity S_λ (1–3) and charge carrier photogeneration quantum yield β(4) vs PDI-1 concentration C in polyimide films: 1-PI-II, 2-PI-III, 3-PI-I, 4-PI-II. Excitation 540 nm, high solvent evaporation rate (substrate temperature 100°C), positive corona.

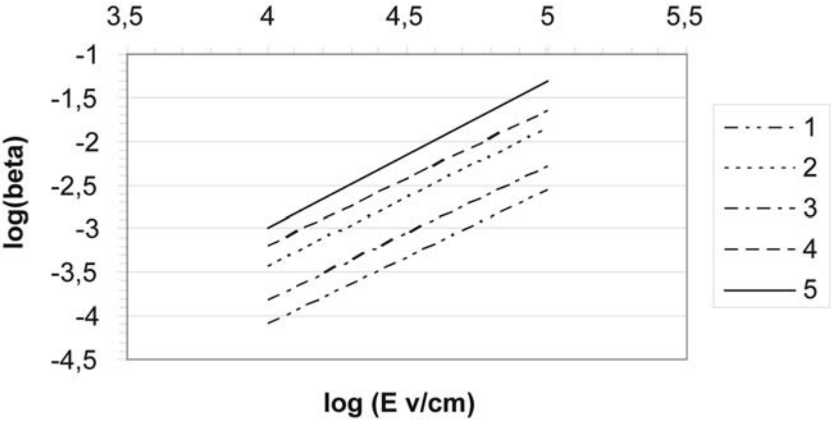


FIGURE 2 Charge carrier photogeneration yield β vs electric field E for various PDI-1 concentrations C in PI-II films (1–1%wt, 2–30%, 3–3%, 4–50%) and PI-II + PEI + PDI-1 blend films (5) (X = 0.5, C = 50%wt). Excitation 540 nm, positive corona charging.

recombination [8] permits to make conclusion that for various PDI contents electron-hole pairs have the same charge space separation $r_0 = 3{,}5$ nm but various initial yield $\phi = 0{,}10$–$0{,}98$ increasing upon PDI concentration. So for fixed electric field ($E = 10^5$ v/cm) the β value increment vs PDI concentration (Fig. 1, curve 4) is due exclusively to initial pair yield ϕ increase. Since after initial charge separation electrons localize inside PDI aggregates (as electron acceptors) the pair space separation r_0 value likely correlates with active aggregate size. So the constant r_0 value implies that the photogeneration occurs presumably with participation of aggregates of definite size (probably of about some tens nanometers).

Spectral dependence of S_λ value for the most sensitive compositions (50% wt PDI content) coincides in main features with the film absorption spectra and have the same peaks as the diluted PDI solution (430, 460, 490, 530–540 nm). Only at the longwave edge (570–600 nm) the S_λ spectral dependence has an additional maximum appearing at high PDI content which is likely connected with aggregate participation in photogeneration process.

PV measurements for composite films are carried out in sandwich cells with transparent ITO and semitransparent Al electrodes. Open circuit voltage (negative sign on the metal electrode) under visible light illumination is Uoc = 1.4 volts, the highest short circuit current ($\lambda = 540$ nm) related to the incident light intensity $Jsc/I_\lambda = 0.8$–1.0 mA/W, the filling factor FF = 0.21–0.25. So the energetic conversion efficiency of PI + PDI composite based cells (for film thickness 0.7–1.0 μ) is about 0.02–0.03%. It is found also that the Jsc value is higher for the illumination through semitransparent Al electrode even without taking into account its transparency that indicates the potential barrier and active photogeneration zone formation on the metal-polymer interface.

The comparison of electrophotographic sensitivities of PI-II + PDI-1 composite films under inhomogeneous excitation by the strongly absorbed light for negative and positive corona charging enables us to find out that the composite films possess presumably p-type photoconductivity in spite of the fact that PDI itself displays n-type conductivity [9]. The electron conducting network is found to be formed in films of PDI-1 doped (up to 50% wt) polyetherimides (PEI of Ultem-1000 type) with no active donor chain groups and less effective dopant aggregation. This conclusion is evidenced also by the electrophotographic measurements under inhomogeneous film excitation for polymer blends involving two polymer components (PI + PEI) in various relative weight ratios X = PI-II/(PI-II + PEI) at high PDI-1 content (50% wt) distributed approximately in equal proportions between polymer components Figure 3.

As it can be seen from Figure 3 for middle X = 0.1–0.5 the PDI-1 doped blend films possess the sensitivity for both signs of corona charging and consequently bipolar transport. For these X values but low PDI-1 content (0.15 % wt, when there is no aggregate formation) the intensive light scattering is observed in blend films that indicates a microphase segrega-

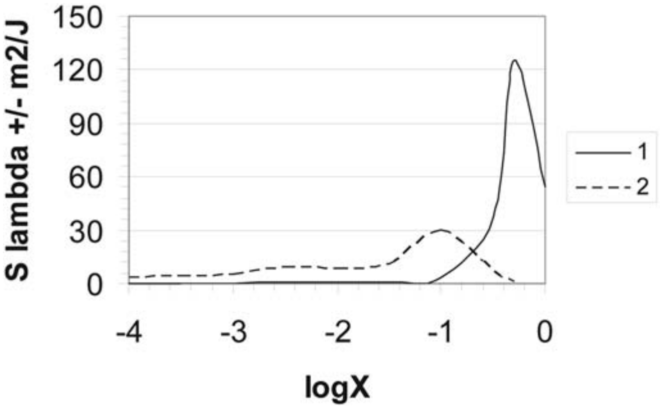


FIGURE 3 Electrophotographic sensitivity S_λ under inhomogeneous excitation ($\lambda = 540\,\text{nm}$) for positive (1) and negative (2) corona charging of polymer blend (PI-II + PEI) films doped by PDI-1 (C = 50%wt) vs relative weight ratio of polymer components X = PI-II/(PI-II + PEI).

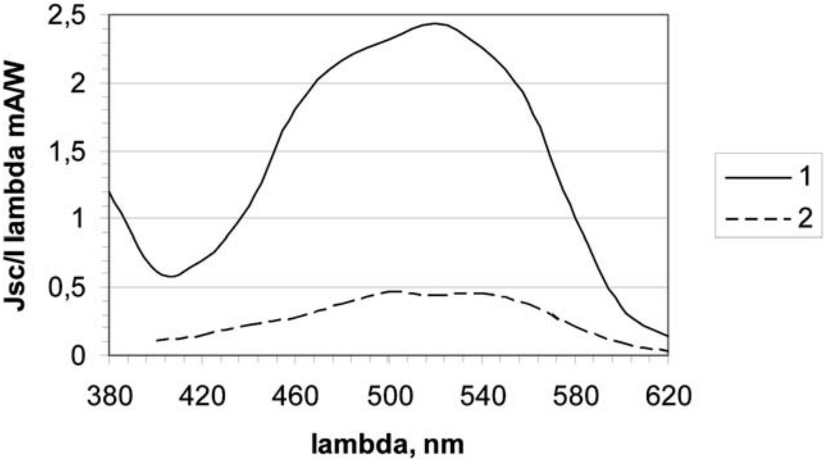


FIGURE 4 Spectral distribution of short circuit current related to the incident light intensity Jsc/I_λ for PV cells based on PDI-1 doped polymer blend (PI-II + PEI) films (relative weight polymer component ratio X = 0.86, PDI-1 content C = 50% wt), excitation: 1 – through ITO electrode, 2 – through Al electrode.

tion of two polymer components due to their partial incompatibility. The microsegregation in heavily doped polymer blend films results in the formation of polymer microregions with n-and p-types of conductivity contacting with each other.

These doped microsegregated blend films are characterized by the highest electrophotographic sensitivity in PDI-1 longwave absorption band (up to 200 m^2/J) and charge carrier photogeneration quantum yield β (Fig. 2, curve 5). Increase of β and improvement of electron transport result in the significant improvement of PV characteristics for sandwich cells based on doped blend films (of thickness 0.5–0.7 μ) under visible light excitation: open circuit voltage Uoc becomes equal to 1,55 volts, highest short circuit current related to incident light intensity Jsc/I_λ = 2.45 mA/W (Fig. 4, curve 1), filling factor determined from photocurrent-voltage cell characteristics becomes FF = 0,31 and so the energetic conversion efficiency increases to 0.1–0.2%.

In this case just in contrast to PI-PDI composites the illumination through ITO electrode is as effective as through the Al electrode if one takes into account its transparency that proves the decrease of metal – polymer interface role in photogeneration process. So the latter occurs through the film bulk. The enhanced Uoc value becomes close to the difference between PI HOMO (5.3–5.5 ev) and PDI LUMO (3.5 ev). So we can suggest that in microsegregated doped polymer blends the bulk p-n microheterojunction formation is possible.

The further improvement of PV characteristics can be achieved both due to rationalized film preparation technology for improvement their morphology and due to extension of cell sensitivity spectral band to the 600–700 nm region by using novel PDI derivatives or additional sensitizers with higher molar extinction coefficients.

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