Photoelectrical and Photovoltaic Properties of Polyimide-Perylenediimide Composites

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Charge carrier photogeneration quantum yields (β), electrophotographic sensitivity (S_{λ}) and photovoltaic characteristics are investigated for films of the organosoluble polyimides (PIs) with double triphenylamine (TPA) units in their chains:



with additives of soluble perylenediimides (PeDIs) of such structure:



at content of latters from 0,5 to 70 % wt. In spite of the large added PeDI content (50-70 % wt) the composite films look homogeneous, without any cloudines, and homogeneously coloured.

Among the composites studied the highest photosensitivity ($S_{\lambda} = 120 \text{ m}^2/\text{J}$) and photogeneration quantum yield ($\beta = 2,5 \cdot 10^{-2}$, $E = 10^5 \text{ V/cm}$) values in the PeDI longvawe absorption band (480-540 nm) are found for PI-II films at maximal content (30-70 % wt) of PeDI-1 which shows relatively low solubility in the chlorinated solvents used. For the PI films with PeDI-2 additive the S_{λ} and β values are found to be much lower ($S_{\lambda} < 20 \text{ m}^2/\text{J}$) for the same additive contents. The PI-I and PI-III films with PeDI-1 additives show some lower photosensitivity ($S_{\lambda} = 50$ and 80 m²/J correspondingly) as compared with the similar PI-II samples.

It is found the essential, more than one order of magnitude, rising of the photogeneration quantum yield β in PeDI-1 absorption band at weak electric fields (E $\leq 10^5$ V/cm) with PeDI-1 content increasing up to highest content used without saturation. The explanation of these experimental data is proposed based on the assumption of interpenetrating network formation of molecular (or nanosize crystaline) PeDI-1 aggregates with n-type conductivity which enter the electron donor-acceptor interaction with donor (double TPA) units of the PI chains.

The preliminary measurements of photovoltaic characteristics of PI-II films with PeDI-1 additives (of thickness $\leq 1-1,5 \ \mu m$) are carried out for sandwich-type cells with transparent ITO and semitransparent Al electrodes: the open circuit voltage U_{OC} = 1,4 V (at visible light excitation intensity I $\leq 5 \ mW/cm^2$), spectral short circuit photocurrent density related to the excitation intensity I_{λ_2} j_{SC}/I_{λ_2} $\leq 1 \ mA/W$, filling factor FF = 0,21-0,25.

Formation of PeDI-1 molecular aggregates is evidenced by observation of molar extinction coefficient ε decrease in dye absorption band { $\lambda_{max} = 540$ nm) with its content C increasing (for C > 10% wt). This decrease is accompanied also by the quenching of PeDI-1 luminescence with increasing its concentration which can be explained also by aggregate formation. Microscopic observations indicate the aggregate size doesn t exceed

 10^{-5} cm (100 nm). Aggregate formation occurs under high enough solvent evaporation rate during the film casting. The strong luminescence quenching of PeDI-1 both in aggregate (C = 50 % wt) and molecular (C = 0,15 % wt) form by PI-II electron donor fragments is observed which is caused by the electron transfer process from PI-II to PeDI-1.

The PeDI-1 luminescence quenching is observed also in polymer blends of PI-II with the other PIs without any efficient electron donor groups (such as polyetherimide (PEI) of Ultem-1000 type) at the different molar relations PI-II/PEI and the constant PeDI-I content (50 % wt). It is found that the PEI + PeDI-1 films display the *n*-type photoconductivity even at addition of essential quantities of PI-II whereas the films of PI-II itself also containing PeDI-1 (50 % wt) possess only the *p*-type photoconductivity. For the molar relations PI-II/PEI (x) > 0,1 and high PeDI-1 content in polymer blends the intense exciting light ($\lambda =$ 540 nm) scattering is observed in the blend films which likely indicates a microsegregation of the polymers resulting in the *p*-*n*-microheterojunction formation. These sentisized polymer blend films are characterized by higher photoelectrical sensitivity than PI-II+PeDI-1 films that results in also the significant improving of photovoltaic characteristics. For sandwich-type cells based on the polymer blends with the same content PeDI-1 added (50 % wt) and with the same electrodes (Al,ITO) and film thickness $d \approx 0.7 \div 1 \mu$ the open circuit voltage U_{OC} becomes 1,55V (visible light excitation), spectral short circuit photocurrent density (for $\lambda = 570$ nm)related to the exciting light intensity $j_{SC}/I_{\lambda} = 2$ mA/W, filling factor FF increases to 0,3. The achieved energy conversion efficiency η related to the incident monochromatic light flux at the maximum of solar spectrum ($\lambda = 550$ nm) is ~ 0.1 %.

These results are an essential progress towards the plastic solar cells based on PIs (η increasing from 0,01-0,02 to 0,1). The further significant increase of η value is possible due to improving the film preparation technology to obtain more homogeneous and thinner PI blend-PeDI films at simultaneous increase of incident light absorption and also to using new PeDI derivatives or additional sensitizers for extension of sensitivity spectral band to the 600-700 nm region.

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