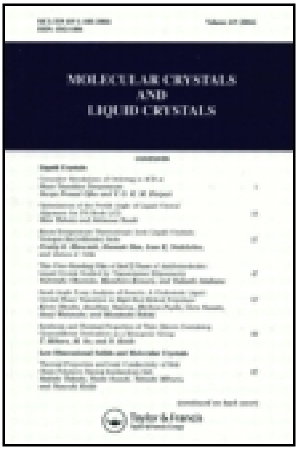

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Effect of Electron Delocalization on Charge Separation in Photoconductive Aromatic Polyimides with Pronounced Electron Donor-Acceptor Interaction

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Effect of Electron Delocalization on Charge Separation in Photoconductive Aromatic Polyimides with Pronounced Electron Donor-Acceptor Interaction

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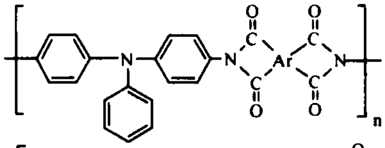
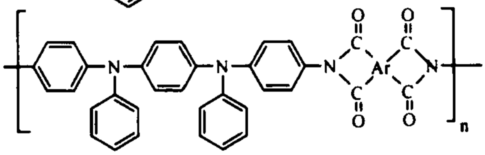
The comparison of charge carrier photogeneration quantum yields β and their field dependencies is carried out for three series of soluble photoconductive polyimides (PIs) based on 4,4′-diaminotriphenylamine (I), N,N′-bis(*p*-aminophenyl)-N,N′-diphenyl-*p*-phenylenediamine (II) and N,N′-bis(*p*-aminophenyl)-N,N′-diphenylbenzidine (III) which differ only by the donor chain fragment size at the same acceptor diimide fragments. In comparison with PIs I series for PIs II and III series the significant increase of β value (by 1–2 orders of magnitude) and initial charge separation distance r_0 in ion-radical pairs (IRP) (from 2 to 3,5–3,8 nm) are found. This increase is due not only to rising density of hole transporting sites but more likely to the efficient delocalization of the positive charge within the extended conjugation system of the donor fragment during IRP formation process. This conclusion is evidenced by the observation of magnetic spin effect (MSF) on photoconductivity which enables to estimate the charge delocalization length in these PIs.

Keywords: Photoconductive polymers; Polyimides; Charge carrier photogeneration; Charge delocalization; Magnetic spin effect

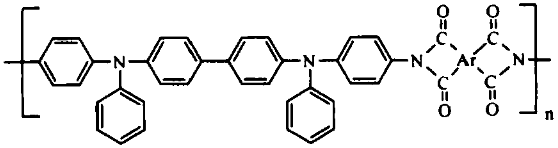
Photoelectrical, luminescent and optical properties of aromatic PIs are determined mainly by the electron donor-acceptor (EDA) interaction in these polymers [1] which chains consist of alternating electron acceptor diimide units and electron donor rests of initial diamines. The actual problem for photoconductive PIs is the development of new approaches to principal improvement of their photoelectrical sensitivity. It's found in the present work that charge carrier photogeneration yield β depends strongly on the delocalization of primarily formed charges within conjugated systems of donor polymer chain fragments. This conclusion follows from the investigation results of three series of PIs with triphenylamine (TPA) and its extended derivatives as donor chain units:



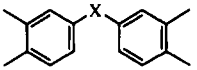
I



II



III

where Ar = 

, X = O (a), – (b), SO_2 (c), CO (d)

The ionization potential (IP) of donor units don't change essentially for these PIs that's indicated by the position of longwave edge in their absorption spectra.

The synthesis of PIs of series I and III is described in [2] and [3] correspondingly. The PIs of II series were synthesized at first time by two-stage cyclopolycondensation of N,N′-bis(p-aminophenyl)-N,N′-diphenyl-p-phenylenediamine with the corresponding tetracarboxylic acid dianhydrides in solution. The PIs of the all three series are soluble in N-methylpyrrolidinone (NMP), 1,1,2,2-tetrachlorethane (TCE) and chloroform. The details of sample preparation and electrophotographic and photoconductivity measurements are described in [2,4]. Magnetic spin effect (MSE) on photocurrent is studied by using the experimental technique described in [4].

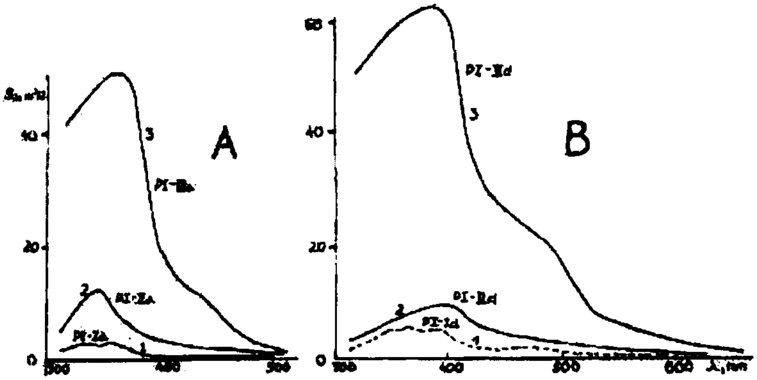


FIGURE 1. Spectra of the electrophotographic sensitivity S_λ for: (**A**) PI Ia (*1*), IIa (*2*) and IIIa (*3*); (**B**) PI Id (*1*), IId (*2*) and IIId (*3*).

It is found the strong, by `1-2 orders of magnitude, increase of electrophotographic sensitivity S_λ for PIs with increasing TPA type donor fragment size at the same acceptor diimide fragment (Fig. 1). The increase of hole transporting site density for PIs with extended donor fragments in accordance with hopping mechanism can not explain the experimental data [5]. It is found however that increase of S_λ for the PIs with extended donor fragments is due mainly to significant, by 1-2 orders of magnitude, increase of the photogeneration yield β (Fig. 2).

Field dependencies of β indicate the charge carrier formation field-assisted thermal dissociation (FATD) of IRP. The treatment of these dependencies based on the Onsager model shows that β increase for PIs of II-III series is due both to the increase of initial yield of IRP Φ_0 and their apace separation r_0 [3]. This implies the delocalization of positive charge over the extended TPA structure For comparison the efficient charge delocalization over the conjugated system of poly(*p*-phenylene vinylene) (PPV) with effective length of about several (6-7) repeating units [5] results in further increasing both the initial IRP yield Φ_0 and charge separation r_0 (Fig. 2, *1*,*5*).

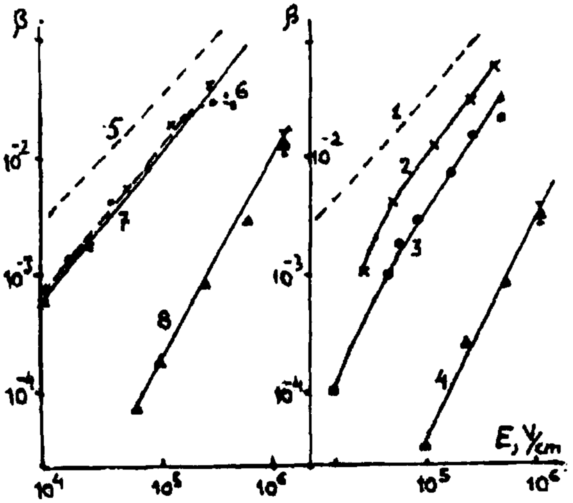


FIGURE 2. Charge carrier photogeneration quantum yield β vs. electric field strength E for PI Ia (*2*), IIa (*3*), IIIa (*4*) and PI Id (*6*), IId (*7*), IIId (*8*) (positive corona charging, excitation $\lambda = 365$ nm) and for PPV films (*1*,*5*) (excitation 436 nm).

This conclusion is strongly supported by the investigation of MSE on photogeneration yield β in these PIs. The photocurrent modulation is found by low external magnetic field H of hyperfine (HF) scale (1-100 Oe) in films of PIs studied of both positive (PIs I) and negative sign (MSE of HFM mechanism). According to HFM mechanism magnetic mixing and demixing of singlet (S) and triplet (T) states of spin-correlated IRP occur in upper dissociative state where exchange interaction (EI) is absent but there is no physical difference between S and T states (energetic degeneracy). In order to have different fates for S and T states and consequently the MSE can be observed it's necessary IRP would spend the certain part of its lifetime in state with low but non-zero EI (more than Zeeman energy $g\mu_B H < 10^{-5}$ eV for HF fields) where small S-T splitting and spin state "checking" takes place (checking level) and that this IRP would have definite probability to return toinitial upper dissociatiative level. As the mutual diffusion of IRP components occurs in a Coulombic well, intrapair distance change due to transition from "checking" to dissociative level is accompanied by the overcome of activation barrier ΔW_1. The spin-independent FATD rate constant is thermally activated also with energy ΔW_2. If ΔW_1 and ΔW_2 parameters are known one can estimate charge delocalisation length l_{del}:

$$2\,e^2/\varepsilon\,(\Delta W_1 + \Delta W_2) \le l_{del} \le 2\,e^2/\varepsilon\,\Delta W_2$$

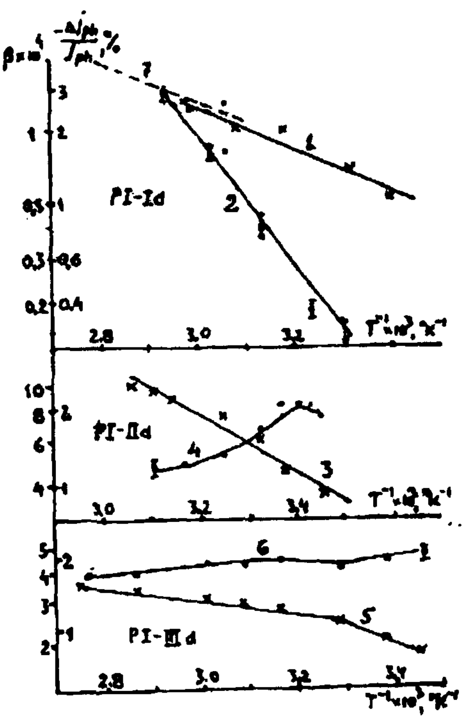


FIGURE 3. Relative change of photocurrent density in magnetic field (H = 1 kOe) $\Delta j_{ph}/j_{ph}$ (*2,4,6,7*) and photogeneration yield β (*1,3,5*) *vs.* T^{-1} for PI Id (*1,2,7*), IId (*3,4*) and IIId (*5,6*) films (sandwich cell with Al and ITO electrodes (*1,3-7*), planar cell with Al electrodes (*2*); excitation in polymer absorption band.

It is found that for PIs of I series negative MSE turns to be thermally activated with ΔW_1 varying from 0,15 to 0,49 eV (the incertainty originates from varying contribution of photostimulated currents which depends on the presence of O_2, excitation spectral region, temperature range [4]) as well as the FATD rate constant (photogeneration quantum yield) with $\Delta W_2 = 0{,}21$ eV (Fig.3, *1*,*2*,*7*).

The obtained l_{del} values are within the range from 0,6-1,2 to 1,9 nm which are less than the charge separation distance r_0 in IRP. For the highly sensitive PIs of II and III series there is no observable thermal activation of MSE (290-390 K); the determined delocalization lengths (3,3 and 4-5 nm for PI IId and IIId respectively) are close to charge separation distances r_0 in IRP which are higher than for PI of I series.

Acknowledgments

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