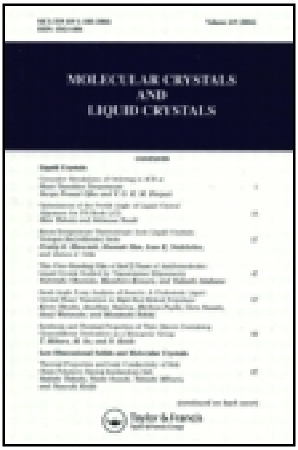

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Photoconductive Properties of Binary Solid Solutions: Thionaphthene-Indole, N-Allyl-Thionaphthene-Indole and N-Isopropyl-Carbazole Doped Polycarbonate

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PHOTOCONDUCTIVE PROPERTIES OF BINARY SOLID SOLUTIONS: THIONAPHTHENE-INDOLE, N-ALLYL-THIONAPHTHENE-INDOLE AND N-ISOPROPYL-CARBAZOLE DOPED POLYCARBONATE*

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Abstract Chemical structure and molecular geometry of dopant molecules can strongly affect the photoelectronic properties of binary solid solutions. The different charge generation mechanisms and mobility resolution in the systems under consideration are clearly correlated to the presence of a crystalline phase. The different solubility of the molecules in the polymer matrix may be ascribed to the different molecular structure and in particular to the presence, in allyl-thionaphteneindole and N-isopropyl-carbazole, of the aliphatic chain which helps homogeneous dispersion.

Keywords Thionaphthene-indole, N-allyl-thionaphthene-indole, N-isopropyl-carbazole, photoconductivity, charge mobility, photoelectric quantum yield.

INTRODUCTION

A lot of work has been done on molecularly doped polycarbonates. Due to the ability to control the densities and the species of the localized states, they are helpful model systems for the interpretation of charge transport mechanisms in amorphous organic solids[1,2]. The possibility of distribution changes of the molecules within the polymer in the solid state, and their effect on the photoconductivity, however, has received little attention. The present study is intended to examine the effect of molecular geometry and chemical structure on the photoelectronic properties of some dopant molecules dispersed in a polycarbonate matrix.

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EXPERIMENTAL

Thionaphthene-indole (TNI) (supplied by Ferrania S.p.A.), N-allyl-thionaphthene-indole (ATNI) (synthesized by the Chemical Institute of the Faculty of Engineering in Bologna), carbazole (Ca) and N-isopropyl-carbazole (NIPC) (from Kodak), were purified by chromatography followed by vacuum sublimation and zone-refining and then used as dopants dispersed in a bisphenol-A-polycarbonate (PC) matrix (Figure 1).

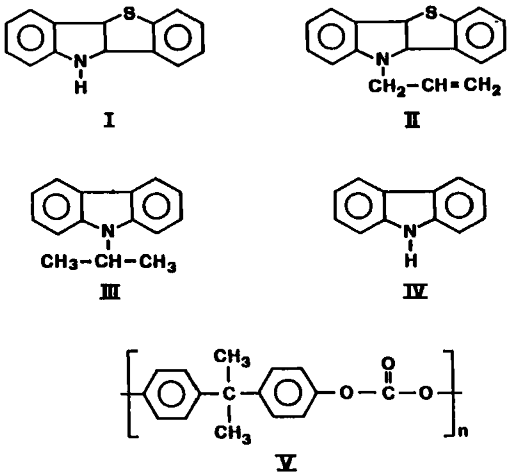

FIGURE 1 Molecular structures. TNI (I), ATNI (II), NIPC (III), Ca (IV) and PC (V).

Each dopant was dissolved with polycarbonate in a common solvent at different "dopant:PC" weight ratios (from 1:9 to 4:6). Films from 2 to 5 μm thick were cast from the solutions and dryed at room temperature and high vacuum ($1{,}3\times10^{-4}$ Pa) for 24-48 hours before being tested.

Transient photoconductivity measurements were done by the time-of-flight (TOF) technique, with a nitrogen laser as the light source[3]; photoconduction action spectra were obtained in the conventional way with a xenon light source and a monochromator[4]. The dopant concentration in the polymer matrix was estimated from its optical density measured with a spectrophotometer and the film thickness derived from the total capacitance ($\varepsilon = 3$) or using a Talystep.

RESULTS AND DISCUSSION

Photoconduction measurements

a) Thionaphthene-indole:polycarbonate (TNI:PC).

In the range 270-370 nm the photocurrent action spectra (with the irradiated electrode positively or negatively biased) exhibit one maximum at 350 nm and antibatic dependence with respect to the absorption spectrum (Figure 2a). Since an intrinsic photocarrier generation mechanism must be ruled out (photon energies of 6-7 eV would be required while the onset of the process is at 370 nm (=3.35 eV)), the antibatic behaviour of the TNI:PC system should be associated with an extrinsic "bulk-generation" mechanism of both electrons and holes, through exciton dissociation at bulk defects.

TOF experiments yielded a photocurrent signal which monotonically decreased with time without any clear indication of the transit time (see inset in Figure 2a).

b) Allyl-thionaphtene-indole:polycarbonate (ATNI:PC).

An exciton-surface mechanism (dissociation of singlet excitons at the surface) is invoked to explain the action spectrum of the photocurrent that follows accurately the absorption spectrum of the film (Figure 2b). The spectrum obtained when the electrode was negatively biased shows an antibatic behaviour with the absorption spectrum, both at low and high voltage and in the whole range of the light intensities used in the experiments. This indicates, in our opinion, that the photocurrent is due to hole generation at the back electrode.

Transient measurements show resolved transit times from which a hole drift mobility of 1×10^{-7} cm^2/Vs, at 4×10^5 V/cm applied field, is derived.

c) N-isopropyl-carbazole:polycarbonate (NIPC:PC).

The photoconductivity action spectra of this system are reported in Figure 2c. The symbatic relation between absorption and action spectra, when the illuminated electrode was positive, at all applied fields used and for a light intensity of 3×10^{13} quanta/cm^{2}s, suggests that in the 250-365 nm spectral region an exciton-surface extrinsic charge generation mechanism is dominant. The spectrum of the negative photocurrent, on the other hand, shows an anti-correlation between the photoconducti-

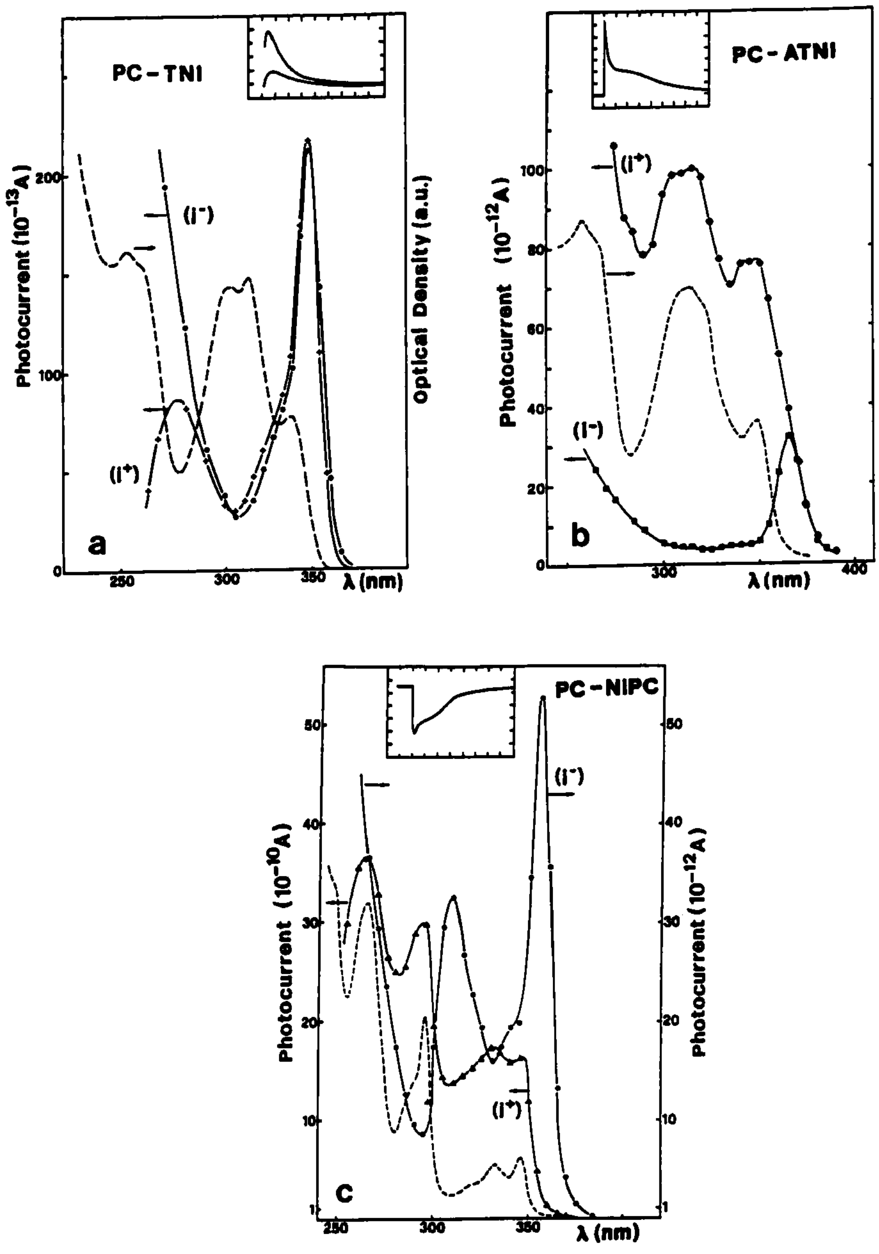

FIGURE 2 Positive (i^+) and negative (i^-) action spectra compared to the absorption spectrum (---) for: (a) TNI:PC (4.5:5.5), F=1.25x10 V/cm; (b) ATNI:PC (4:6), $F=1.0\times10^5$ V/cm; (c) NIPC:PC (4:6), $F=1.2\times10^5$ V/cm. The photocurrent is normalized to an incident flux of 10^{13} quanta/cm^2s. The insets refer to a typical photocurrent transient signal.

vity and the optical absorption spectrum, denoting hole generation at the back positive electrode. The relationship between photocurrent and voltage ($I_{ph} \propto V^{n}$ with n=2.1) and between photocurrent and light intensity ($I_{ph} \propto I^{n}$ with n=0.6) can be explained assuming optical release of injected charges trapped in the bulk, due to their interaction with excitons[5,6].

Moreover, films of NIPC:PC solid solution show resolved transit times in TOF experiments. The hole drift mobility, calculated directly from the photocurrent signals, is 3×10^{-6} cm^2/Vs at 6×10^{5} V/cm.

Morphological aspects

When the concentration of TNI in the PC matrix is higher than 6-7%, the film samples become opaque suggesting a phase separation in the solid solution. In Figure 3 the x-ray diffraction pattern of a TNI:PC film (3:7 weight ratio) compared to PC alone demonstrates the presence of a crystalline phase in the TNI:PC system; the relatively sharp diffraction lines at d-spacing of 11.75, 5.81 and 3.94 Å observed are in agreement with the crystallographic parameters of the TNI single crystal[7].

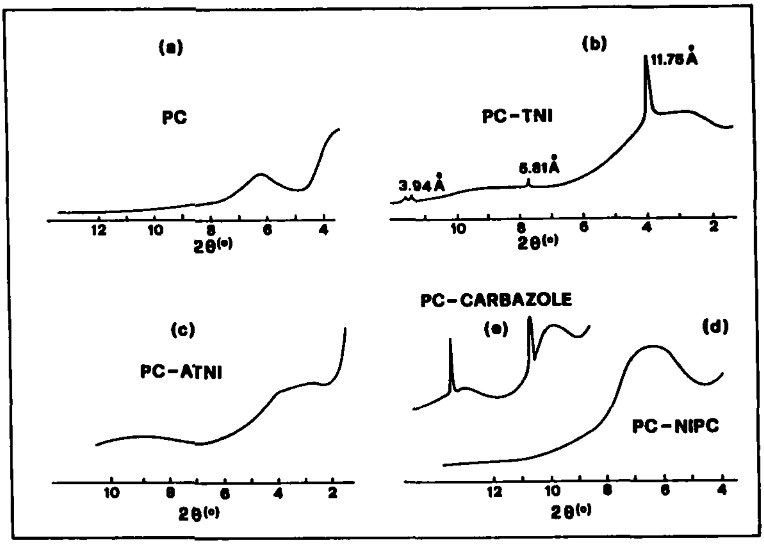

FIGURE 3 X-ray diffraction patterns of the film samples. (a) PC alone, (b) TNI:PC (3:7), (c) ATNI:PC (7:3), (d) NIPC:PC (6:4) and (e) Ca:PC (1:9)

The substitution of an H atom in the -NH (indole) group with an aliphatic chain (Figure 1) confers to the ATNI:PC system a completely different behaviour compared to the TNI:PC parent system. Films of ATNI:PC, in fact, show a completely homogeneous amorphous phase (Figure 3) and a good solubility even for ATNI concentration as high as 70% in weight. Also for NIPC:PC films the amorphous character shown in Figure 3 is confirmed by the good transparency and solubility even for NIPC concentrations up to 60-70% in weight.

Photoelectric quantum yield

The photoelectric quantum yields (Φ), taken at the photocurrent maximum (λ_{Imax}) and at a constant field of $1x10^{5}$ V/cm, are reported in Table I. The different quantum yields obtained in the systems under investigation may be correlated to the different charge carrier generation mechanisms involved.

TABLE I Photoelectric quantum yields of TNI,ATNI and NIPC in PC. Φ(carriers/quantum)

Samples	Φ^{+}	λ_{Imax}	O.D.$_{max}$
TNI:PC (4.5:5.5)	$1.4x10^{-3}$ ($=\Phi^{-}$)	335 nm	1.31
ATNI:PC (4:6)	$6.3x10^{-5}$	348 nm	3
NIPC:PC (4:6)	$8.3x10^{-4}$	347 nm	3

The most efficient mechanism seems to be the bulk generation process occurring in the TNI:PC system. On the contrary, the exciton-surface generation mechanism, inherent in the systems ATNI:PC and NIPC:PC, seems to be less efficient.

CONCLUSIONS

We have shown that the chemical structure and molecular geometry of dopant molecules can strongly affect the photoconductive properties of binary solid solutions. The different charge generation mechanisms and mobility resolution are clearly correlated to the presence or the absence of a crystalline phase within the polymer matrix. The different solubility of the dopant molecules may be ascribed to their different molecular structure and in particular to the presence, in NIPC and ATNI, of the aliphatic chain, which helps homogeneous dispersion. These considerations are confirmed by x-ray analysis on the system carbazole:polycarbonate (Ca:PC) (Figure 3). Carbazole, which has no aliphatic chain like TNI, gives rise, in the matrix, to a crystalline phase.

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