Photoconductivity of sensitized poly(*N*-ethyl carbazole)methane with 2,4,7-trinitrofluorenone

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Photoconductivity of poly(*N*-ethyl carbazolyle)methane was greatly enhanced in the visible region by the addition of a small amount of 2,4,7-trinitrofluorenone having a molar ratio of monomer:dopant from 1:0.06 to 1:0.3. The current–voltage characteristics were studied in the visible wavelength range, and the current increased superlinearly with the increase of doping level. The activation energies for dark and photoconductivity are 0.244–0.202 eV and 0.238–0.194 eV, respectively, at different doping levels. The photoresponse shows two charge transfer bands corresponding to two transitions of the complex.

(Keywords: poly(*N*-ethylcarbazolyle)methane; 2,4,7-trinitrofluorenone; doping; conductivity; activation energy; space charge limited current; charge transfer complex)

INTRODUCTION

In continuation of our research[1-3] on photoconducting polymers, poly(*N*-ethyl carbazolyle)methane (PNECM) was sensitized with an organic electron acceptor, 2,4,7-trinitrofluorenone (TNF)[4] forming a charge transfer (CT) complex. The maximum photoresponse in the system PNECM:TNF was reached at a 1 (monomer):0.4 molar ratio. The high photoresponse of this system in the visible region made it a good photoconductor. The synthesis and electrical and opto-electronic properties of pure PNECM have been reported earlier[3]. The aim of the present paper is to report investigations on PNECM sensitized with TNF.

EXPERIMENTAL

TNF was purified by repeated cyrstallization from acetic acid and by vacuum sublimation. Doped films were prepared by mixing dilute solution of PNECM and TNF in tetrahydrofuran (THF), followed by pouring the mixture over SnO_2, Nesa conducting glass plate and allowing the solvent to evaporate[2,3]. For undoped thin films the same procedure was adopted but in this case the mixing step was omitted.

The steady-state dark and photoconductivity and spectral responses were investigated under vacuum (10^{-5} Torr) in the sandwich configuration[2,3,5]. The conductivity measurements were made using a Keithly electrometer (610C, USA). The photocurrent was measured using a 600 W, 230 V tungsten–halogen lamp as a light source with an i.r. filter. The spectral response was measured using a high intensity monochromator (CEL, HM 104), a photon counter (CEL) and an electrometer, from which the normalized graph was obtained. The intensities at each wavelength were calibrated with a radiometer (CEL SM 204). The absorption spectra of the thin film samples were investigated with a Carry 17-D spectrophotometer in the visible range.

RESULTS AND DISCUSSION

Current–voltage characteristics

The current–voltage characteristics of the sensitized samples were studied under dark as well as under illuminated conditions (120 mW cm^{-2}). *Figures 1* and *2* show a typical set of current–voltage characteristics for the different doping levels of the PNECM:TNF system. It is observed that the current–voltage curves are highly non-linear both in the dark and light. When the current–voltage curves were plotted on log–log scale some peculiar features were revealed. It is seen from *Figure 1* that up to 300 V (thickness of the film 32 μm), the plots are linear with the decrease of doping level after which the curves are superlinear. The superlinearity indicates that the current transport is space charge limited[6]. Above 300 V the current-voltage characteristics can be explained by the shallow traps[7], due to the presence of oxidized impurities, while above 600 V the characteristics can be explained by the trap-fill limit[8,9] current. The nature of the photo current–voltage plot as shown in *Figure 2* is almost similar to that for the dark current–voltage plot except that optical detrapping occurs at above 150 V instead of 300 V (in dark). Thus, light has a greater effect on the current and space-charge limited current increases possibly due to effective detrapping by light. The photocurrent increases linearly below 150 V and then starts to increase superlinearly above 150 V. Thus the number of photocarriers increases with increasing applied voltage because the number of carriers which escape from recombination centres increases by lowering the potential barrier with increasing applied voltage. In the presence of light the effect of the doping level to geminate recombination is greater. Hence superlinearity in the current–voltage plot was observed.

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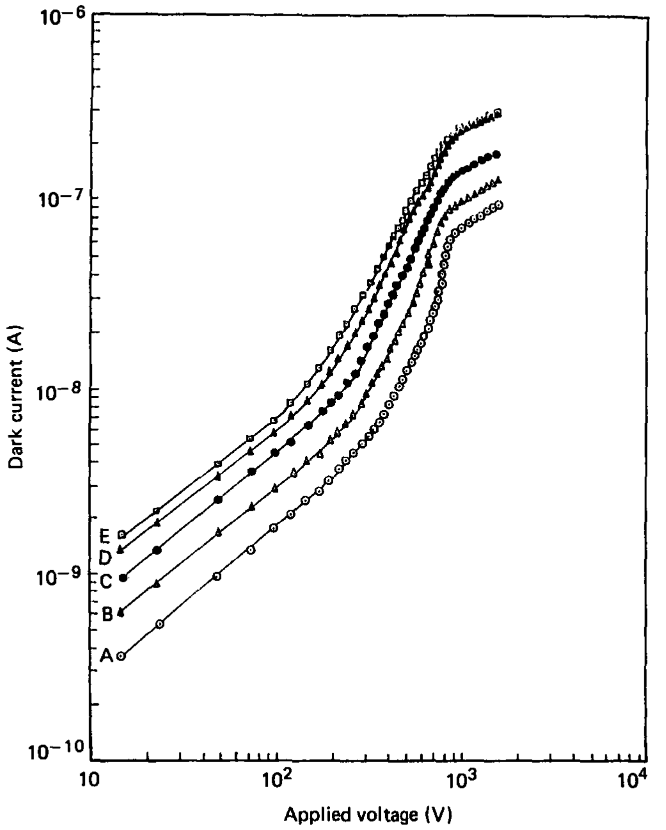

Figure 1 Current–voltage characteristics of PNECM:TNF: A, 1:0.06; B, 1:0.08; C, 1:0.1; D, 1:0.2; E, 1:0.3 at room temperature (300 K) and thickness 32 μm

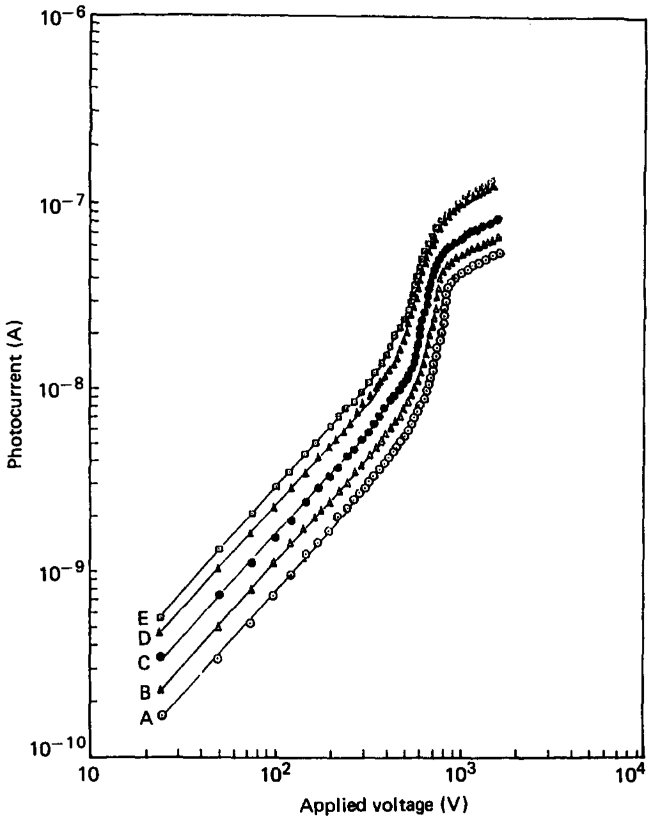

Figure 2 Dependence of photocurrent in PNECM:TNF (A–E as in *Figure 1*) on applied voltage at room temperature (300 K) and a fixed intensity of illumination 120 mW cm^{-2} (film thickness 32 μm)

Doping level in PNECM

The dependence of the current on the doping level (expressed as mol% dopant per mole monomer) at a constant applied voltage of 150 V and intensity of illumination 120 mW cm^{-2} is shown in *Figure 3*. It is noted that maximum value of photoresponse appears at the molar ratio 1 (monomer unit):0.4 (TNF).

Photocurrent–intensity variation

Photocurrent (I_p)–intensity (I) variation of PNECM:TNF film has been investigated for different doping levels. Photocurrent plotted against I on log–log scale as shown in *Figure 4* is linear. The I_p is proportional to $I^{0.65}$. Thus the photocurrent of the charge transfer complex is due to bimolecular recombination[10,11].

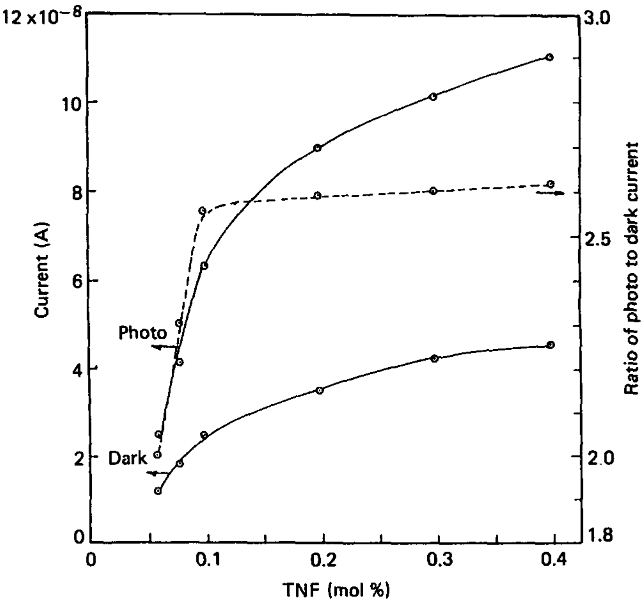

Figure 3 Current *versus* doping level in PNECM:TNF (virgin PNECM film of thickness 32 μm, current 10^{-10} A

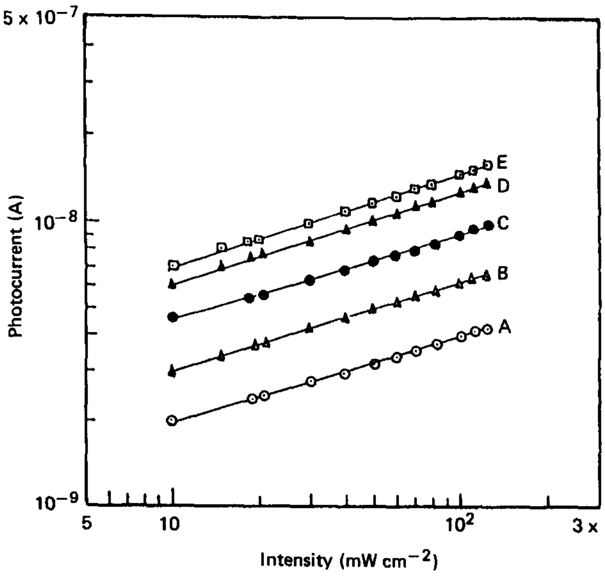

Figure 4 Photocurrent versus light intensity in PNECM:TNF (A–E as in *Figure 1*). Film of thickness 32 μm and applied voltage 100 V at room temperature

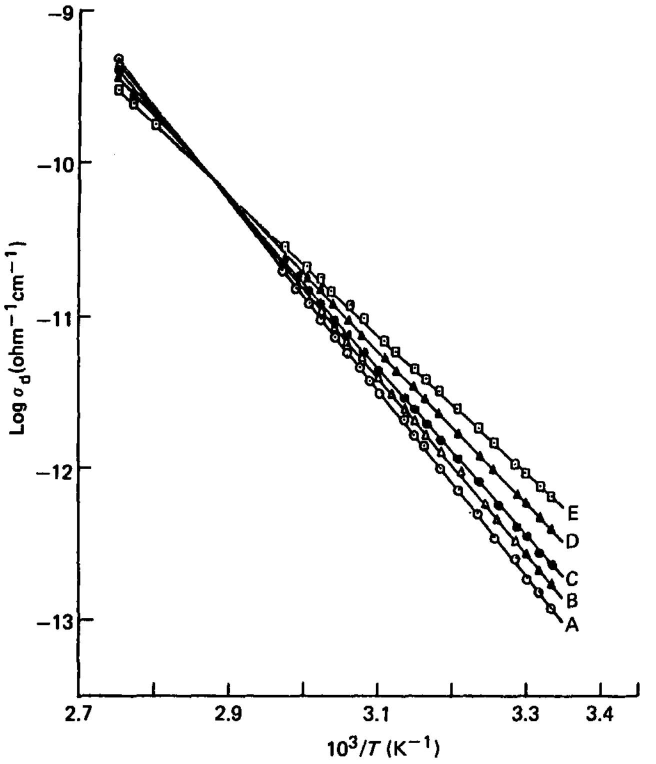

Figure 5 Dark conductivity variation with temperature of PNECM:TNF (A–E as in *Figure 1*). Film of thickness 32 μm

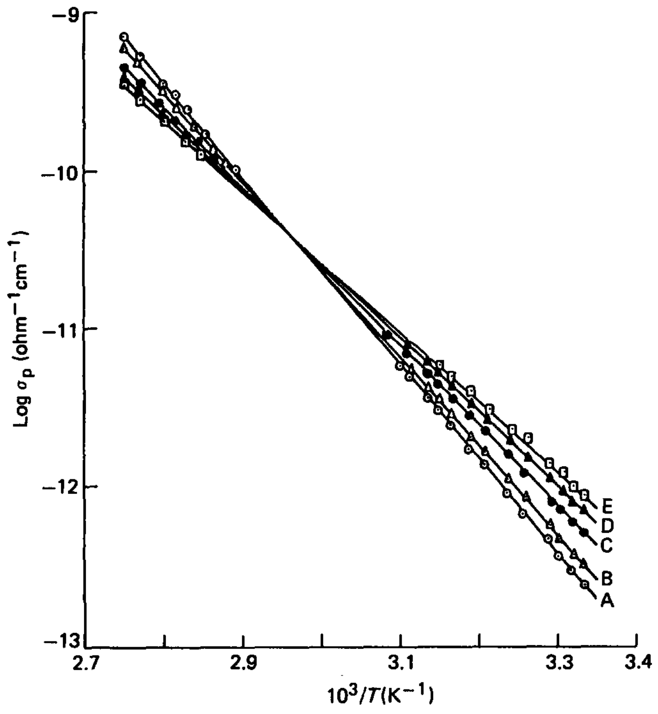

Figure 6 Temperature dependence of photoconductivity of PNECM:TNF (A–E as in *Figure 1*). Film of thickness 32 μm at fixed intensity of illumination (120 mW cm^{-2})

Temperature dependence of conductivity

In *Figure 5*, the temperature dependence of dark conductivity σ_d in PNECM–TNF system is shown. The majority carriers appear to be electrons by the thermal probe method. The temperature dependence of photoconductivity, σ_p, in the PNECM–TNF system is shown in *Figure 6*. The relation between the dark and photoconductivity and the reciprocal of temperature in all the samples including pristine PNECM obeyed the expression $\sigma_d \propto \exp(-E_{ad}/kT)$ and $\sigma_p \propto \exp(-E_{ap}/kT)$ respectively. The activation energies[3] of dark conduction and photoconduction of pristine PNECM were 0.34 and 0.3 eV, respectively, having electrons as majority carriers. Starting from these values, the activation energies of dark and photoconduction in doped PNECMs gradually decreased with the increase of TNF content. *Figures 5* and *6* show the log σ_d and log σ_p *versus* T^{-1} plots in the PNECM–TNF system. The apparent activation energies, E_{ad} and E_{ap}, obtained from *Figures 5* and *6* are shown in *Table 1*. In this system the activation energies gradually decrease with the increase of dopant content.

Spectral characteristics

The absorption spectrum of the complex in a solid film for different PNECM:TNF ratios along with the optical absorption spectrum of PNECM solid film are shown in *Figure 7*. Two CT bands have been observed, and are

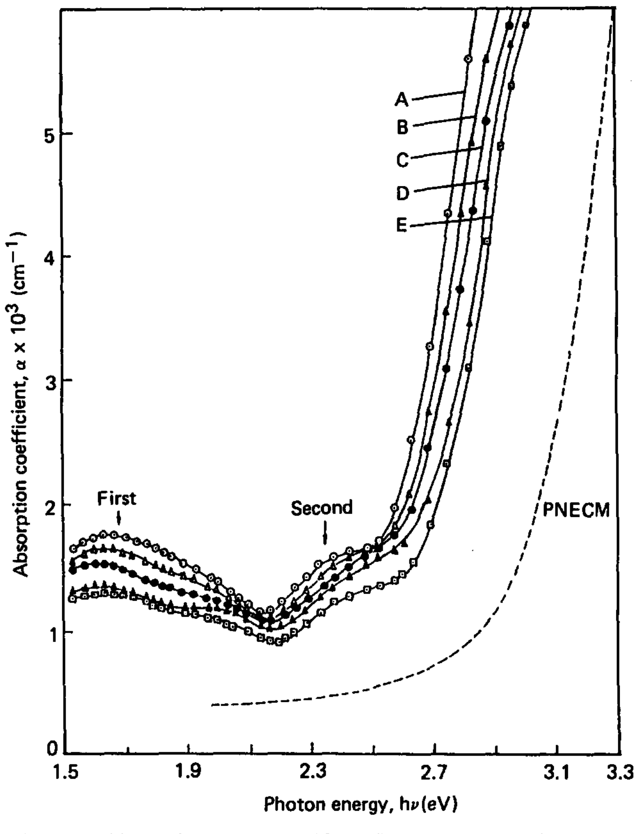

Figure 7 Absorption spectrum of PNECM:TNF (A–E as in *Figure 1*) and PNECM measured in film at room temperature

Table 1 Parameters obtained for various PNECM:TNF molar ratios

PNECM:TNF	Dark activation energy (eV), E_{ad}	Photo-activation energy (eV), E_{ap}	Absorption maxima (eV) First transition	Second transition
1:0	0.34	0.30	–	–
1:0.06	0.224	0.238	1.68	2.47
1:0.08	0.229	0.225	1.66	2.45
1:0.1	0.218	0.211	1.65	2.44
1:0.2	0.211	0.200	1.63	2.42
1:0.3	0.202	0.194	1.62	2.40

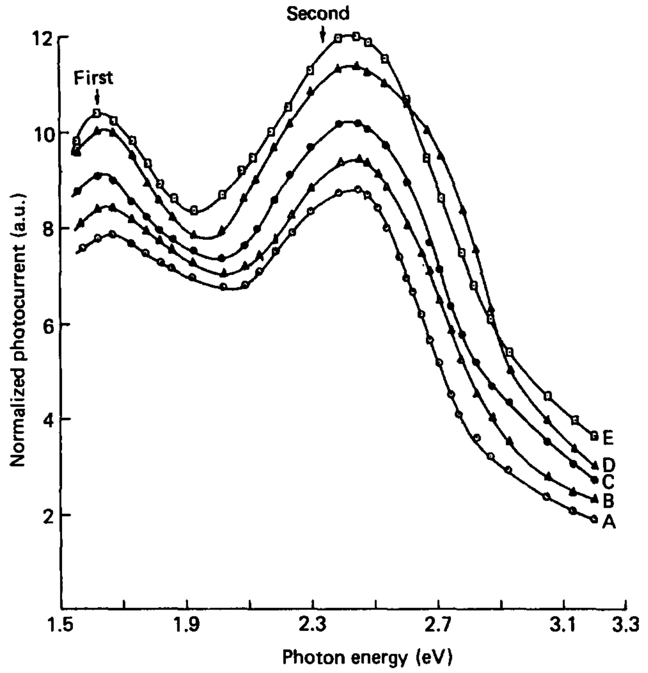

Figure 8 Spectral dependence of photocurrent in PNECM:TNF (A–E as in *Figure 1*). Film thickness 32 μm at room temperature

designated as first and second transitions. Absorption maxima of these two transitions coincide with photoresponse maxima with respect to photon energy, which reveals two maxima in photoresponse as shown in *Figure 8*, a stronger one (second) at 2.4 eV due to the CT complex and a weaker one (first) at 1.6 eV, possibly another kind of CT complex. Pristine PNECM does not show any maxima in the absorption band. It can be concluded that the appearance of the weak peak (first) in the photoresponse curve is not due to the presence of any impurities.

Efficient photoconductivity in a polymer can be originated through CT complex formation, as established by earlier workers. It is probable that excitation of the PNECM:TNF CT complex facilitates the generation of carriers. In this way, the complex acts as an internal charge injector into the PNECM system. The photocurrent of the PNECM:TNF CT complex increases faster at a low concentration of TNF in comparison to the dark current. This causes a sharp rise in the ratio of photo–dark current up to a concentration of TNF of 0.1 mol%, after which the ratio becomes more or less constant.

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