

## Photoconductivity of polymers doped with some charge transfer complexes

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**Abstract.** Photoconductivity of polystyrene doped with anthracene as a donor and 7,7,8,8-tetracyanoquinodimethane as acceptor was investigated by studying the photocurrent ( $I_{ph}$ ), the dark current ( $I_d$ ) and the sensitivity  $I_{ph}/I_d$  as the acceptor concentration changed. For this purpose a novel liquid cell was designed and successfully used for measurements. It was found that polystyrene films containing (1:10) donor-to-acceptor ratio has the greatest sensitivity as the applied charging voltage equals 0.25 volt.

**Keywords.** Photoconductivity; doped polystyrene; sensitivity; applied changing voltage.

### 1. Introduction

Photoconductivity measurements of samples having a high resistivity need special techniques. Such techniques are:

(a) Damber technique (Akamatu and Kuroda 1963; Hayashiy *et al* 1966; Gill 1972) by simply applying a voltage across an organic material sandwiched between two transparent or semi-transparent plates. When one of the electrodes is illuminated, carriers are generated on the surface and diffuse into the material to create a potential difference between sample and the illuminated electrode, and (b) Xerographic technique: (Mort and Emerald 1974; Williams *et al* 1975; Degorski and Kryszewski 1975a). There are two xerographic techniques commonly in use. The first involves corona charging of the surface of a polymer film cast on a suitable conductor substrate. The photoconductivity is measured by monitoring the decay in surface potential after exposure to a pulse of light. In the second method, the sample is covered by a thin layer of a highly efficient photogenerating material. The rate of decay in the surface potential provides the required information.

The technique used in the present study is based on these techniques and involves applying a liquid cell (Frankevich and Sokolik 1967; Frankevich 1971) containing a thin film between two water electrodes. The water acts as a transparent electrode (as in the Damber technique) and a parallel condenser is used to charge the electrodes instead of the corona charging (as in the xerographic technique).

The rate of discharge throughout the films on applying an external illumination and in the dark has been recorded. The two discharge curves intercept each other at a point where the surface voltage is the same. The measured difference between the slopes gives information about the photoconductivity of the material used.

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The samples used are taken from polystyrene films doped with anthracene (Anth) (donor) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) (acceptor). The specific properties of charge transfer (CT) complexes arising from electron transfer between donor and acceptor molecules enable these systems to be characterized by photoconductivity.

### 1.1 General formulation of the discharge characteristics

The surface potential ( $V_s$ ) decays with exposure  $X$  due to the flow of photocurrent under inconstant voltage conditions. The photocurrent is controlled by two limiting mechanisms:

(i) At high potentials and low light intensity, the number of free carriers transported per transit time is small compared to ( $CV_s$ ), where ( $C$ ) is the receptor capacitance. Thus the current is emission-limited.

(ii) At a lower potential and high light intensity, the ( $CV_s$ ) of the charge required to discharge the photo-receptor could traverse the sample in one transit and the current becomes space-charge limited. The emission-limited current  $= J_e = eN_c$  where  $e$  is the charge on a carrier and  $N_c$  is the number of carriers emitted per unit time per unit area.

The decay time ( $t$ ) of the emitted photocurrent is proportional to the produced photocurrent and its value can be given by subtracting the two slopes ( $V_s$  against  $t$ ) and ( $V$  against  $t$ ) in the dark and in illumination.

### 1.2 Measuring procedure

In figure 1, curve 1 is related to the film discharge due to the dark current ( $J_s$ ) and curve

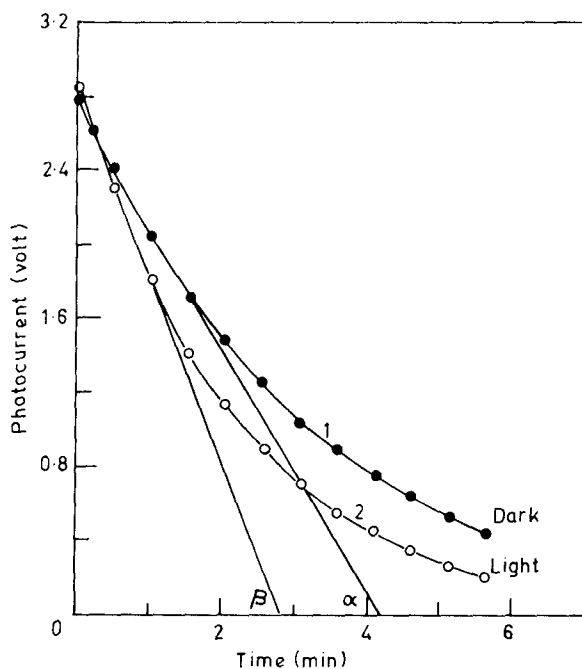


Figure 1. Photocurrent vs decay time.

2 is due to both the photocurrent on illumination and the dark current at  $t = t_1$  where the surface voltage has the same value.

The photocurrent intensity is then proportional to  $(\tan \beta - \tan \alpha)$ .

## 2. Experimental

In the present work, the films ( $30\mu$  thickness) of polystyrene doped with anthracene and TCNQ as donor and acceptor respectively, were prepared according to Degorski and Kryszewski (1975a). Figure 2 shows the schematic diagram of the apparatus used to investigate the photoconductive properties of the CT complex formed within the film. It consists of four different parts; a light source (I), a liquid cell (II), a charging circuit (III) and a measuring unit (IV). The light source (I) consists of a 200 W tungsten lamp a, for illumination of the first surface of the film, a collimating lens b, to make the illumination homogeneous, and a slit c, to minimize the stray light and acts also as a shutter. The liquid cell (II) consists of two hollow teflon parts d, f, one of them provided with a quartz window, the two parts tightly enclosing the film e. One of the two parts is filled with water as a transparent medium and acts as a first electrode. The other part is covered with a copper plate covered with graphite to make good contact with the other surface of the film. The charging circuit (III) consists of a charging unit and a capacitor (C). The measuring unit (IV) is a DC multimeter type TM9BP used for measuring the decay voltage.

## 3. Results and discussion

In order to investigate the capability of the system for photoconductivity measurements (anthracene, TCNQ) doped polystyrene films were used. They are known to form a CT complex in the excited state which interacts with anthracene in the ground state, producing free electrons. To study the mechanism of CT complex formed, the difference in absorption spectra of Ps + TCNQ and Ps + TCNQ + Anthracene were recorded as in figure 3. This figure shows a decrease in the absorption of anthracene as the TCNQ concentration was increased. A slight red shift in the absorption of the TCNQ of about 10 nm has been observed. This can be attributed to the formation of ionic TCNQ.

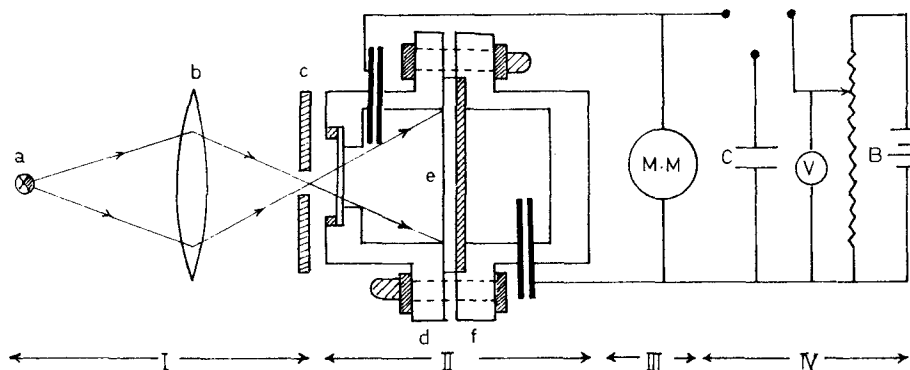


Figure 2. Schematic diagram of the apparatus used.

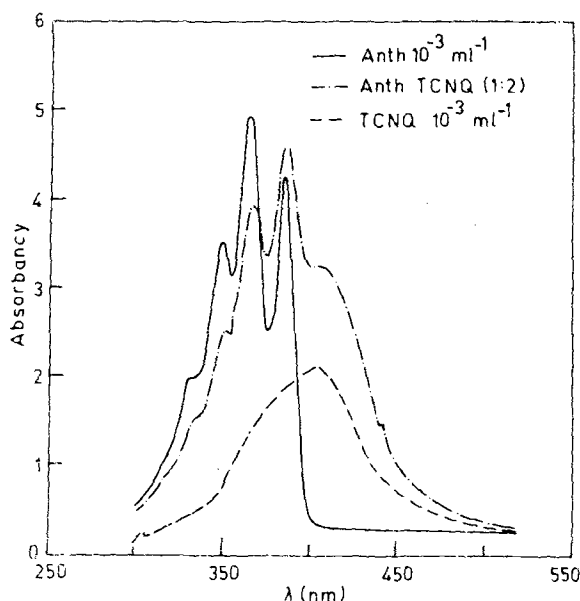
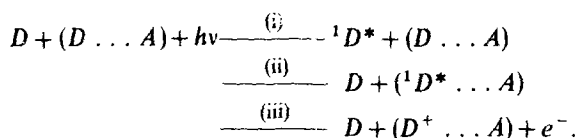


Figure 3. Absorption spectra (Anth-anthracene).

radical anion absorbs light strongly at 4200 Å, while neutral TCNQ absorbs at 3950 Å. Our results indicate the formation of a CT complex. A proposed mechanism for the formation of free electrons in similar systems was given as (Degorski and Kryszewski 1975a)



Thus it follows that the most probable mechanism of quenching is energy transfer from unbound anthracene to anthracene molecules bound in the complex. The excited acceptor centre then undergoes deactivation as a result of which charged species may arise.

In order to investigate the validity of the apparatus for measuring the photoconductive properties of the above materials which are thought to form CT complexes, TCNQ and anthracene, different acceptor concentrations were used to prepare the films, while donor concentration remains constant. The measured values of the photocurrent ( $I_{ph}$ ) and the dark current ( $I_d$ ) in arbitrary units as well as the ratio between them are given in table 1.

It can be seen that  $I_d$  is proportional to the applied voltage of discharge. This is in agreement with Childs law (Degorski and Kryszewski 1975b). The  $I_d$  was found to have irregular values with increasing acceptor concentration. It has maximum value as the concentration ratio reaches (1:10).

**Table 1.** Relative photocurrent intensity for polymer donor-acceptor systems at different conditions.

Anthracene	Concentration ratio mM		Charging voltage (V) in volts	$I_{ph}$ arbitrary units	$I_d$	$I_{ph}/I_d$
	TCNQ					
1	5	0.25	0.09	0.08	1.13	
		1	0.08	0.021	0.38	
		3	0.41	0.68	0.6	
1	10	0.25	0.38	0.22	1.73	
		1	0.84	0.93	0.9	
		3	0.5	2.5	0.2	
1	15	0.25	0.9	0.18	5	
		1	1.2	0.4	3	
		3	0.58	1	0.58	

The observed values of  $I_{ph}$  increase as the acceptor concentration ratio is increased, while it irregularly changed with discharge voltage.

From the above conclusions it is impossible to select the most suitable photoconductive system. We therefore attempted to calculate the sensitivity of each system. At different values of  $V$  we took the known relation of sensitivity as a signal-to-noise ratio. The calculated values of  $(I_{ph}/I_d)$  (table 1) clearly indicate that the system (Ps: 1 anthracene 10 TCNQ) at discharging voltage of 0.25 V is the most sensitive one.

Generally the system used was very simple and gave reliable information about the photoconductive properties of plastic films doped with  $\pi$ - $\pi$  complexes. Further work is being planned to investigate other systems in the hope of finding one which can be used as a solar cell.

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