

Photoconductivity of Poly((E,E)-[6.2]paracyclophane-1,5-diene) and Its Complex with TCNE

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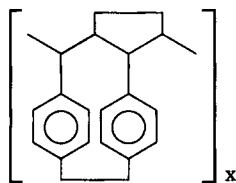
SYNOPSIS

Steady-state photoconductivity measurements carried out for poly((E,E)-[6.2]-paracyclophane-1,5-diene) pure and sensitized with tetracyanoethylene show that doping causes a significant increase of the photoconductivity. This is due to an increase of both the hole mobility and the photogeneration efficiency. The shape of the spectral characteristic is explained by the possible existence of two paths for charge-carrier photogeneration connected with absorption of the light by the cyclophane unit for shorter wavelengths or by CT complex for longer wavelengths. For an electric field lower than 10^6 V/m, the photocurrent exhibits an ohmic field dependence, and for higher fields, it becomes proportional to $F^{1.5}$.

INTRODUCTION

Interest in photoconducting polymers is connected with an increasing need for low-cost, easy-to-process and easy-to-form large-area materials, which could be applied in the xerography or solar cells. Although many photoconducting polymers are known, there are only a few examples of application of such materials. This is because it is not easy to find soluble polymer that exhibits large photogeneration efficiency, large charge-carrier mobility, chemical stability, and good mechanical properties.

It seems that poly((E,E)-[6.2]paracyclophane-1,5-diene) (PDE), a recently synthesized polymer,¹ meets these requirements:



It is easily soluble in, e.g., dichloromethane and chloroform, and flexible, transparent films may be cast from these solvents.

As has been shown,² PDE reveals high mobility in comparison with other amorphous, photoconducting polymers. The hole mobility in PDE is several times higher than is the mobility in poly(*N*-vinylcarbazole) measured under the same experimental conditions. Such high mobility is probably connected to a cofacial alignment of bridged aromatic rings pendant to the polymer backbone leading to delocalization of generated charge carriers. The existence of such a cooperative electronic effect in PDE was confirmed by fluorescence spectroscopy and ESR.³

Oxidation of PDE by exposure to iodine results in material that reveals high conductivity, which again can be explained by the existence of aligned, interactive paracyclophane segments that have been oxidized to radical cation salts. These small segments are of random length and orientation that can limit the bulk conductivity of such material.³ In this work, we present the results of photoconductivity measurements carried out for PDE pure and sensitized with a low molecular weight acceptor.

EXPERIMENTAL

Preparation of Pure and Doped PDE Films

Both pure and tetracyanoethylene (TCNE)-doped films of PDE were cast at room temperature under slow evaporation conditions from dichloromethane

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solution. The concentration of the dopant was varied in the range 0–6 wt %; at higher concentration, TCNE precipitates in a course of film casting. Films of ca. 5–15 μm are transparent and exhibit good mechanical properties. Films of pure PDE are colorless, whereas films that contain TCNE are dark blue. Visible and near ultraviolet spectroscopy of pure samples shows relatively strong absorption for wavelengths shorter than 380 nm, which is typical for polymers that contain large aromatic groups. Films doped with TCNE reveal an additional, broad charge-transfer (CT) band with maximum at 570 nm.

For photoconductivity measurements, aluminum electrodes were evaporated on both sides of the samples. Reference glass plates were evaporated simultaneously to determine the transmission of the electrodes. For comparative measurements, the films of a well-known polymer photoconductor, poly(*N*-vinylcarbazole) (PVK), were prepared by casting from dichloromethane solution onto Nesa glasses or onto thin aluminum plates.

Photoconductivity Measurement Procedure

The samples were placed in a vacuum chamber with quartz windows. The upper semitransparent electrode was illuminated with a xenon lamp XBO-100 using a prism monochromator (Carl Zeiss Jena). The incident light intensity was determined using CA-1 (Kipp & Zonen) thermopile situated in the sample position. Spectral response characteristics were obtained by keeping the photon flux constant. Electric currents were measured by a Keithley 616 electrometer. All the measurements were carried out at room temperature. The results were expressed by the effective gain coefficient G , which is the ratio of the number of photogenerated charge carriers collected by the electrode per time unit to the photon flux effectively absorbed by the polymer films:

$$G = \frac{(j_{ph} - j_d)}{e(1 - T)N_0} \quad (1)$$

where j_{ph} is the photocurrent density; j_d , the dark current density; T , the transmission of the polymer film; and N_0 , the incident photon flux (corrected for the absorption of the electrode).

Measurements of spectral response characteristics and of electric field dependencies were performed as follows: After a voltage was applied to the sample, a so-called absorption current was observed for a long time (typically longer than 0.5 h), until the dark current was very low, almost constant.

Then, the photocurrent was measured for 15 min in order to reach a steady-state value. After the light was turned off, a decay of the current was observed. When it reached the dark current level, the measurement procedure was repeated for another wavelength or another electric field.

Light intensity dependencies were carried out for two different slit widths of the monochromator yielding two different maximum photon flux $I^{100\%} = 8 \cdot 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ and $I^{100\%} = 8 \cdot 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$. Then, the incident photon flux (I) was changed within these two ranges using gray filters.

Xerographic discharge tests were carried out for pure PVK films on aluminum plates and for PDE films doped with 4% TCNE using Dyntest-90 set (ECE GmbH). As a light source, an HBO-200 mercury lamp with different interference filters was used.

RESULTS

Pure PDE samples reveal relatively low (about $8 \cdot 10^{-20} (\Omega \text{ cm})^{-1}$) conductivity in the dark. The photoconductivity of these samples is also weak, and it decreases with increasing wavelength (Fig. 1). For maximum photon flux ($8 \cdot 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$) and ex-

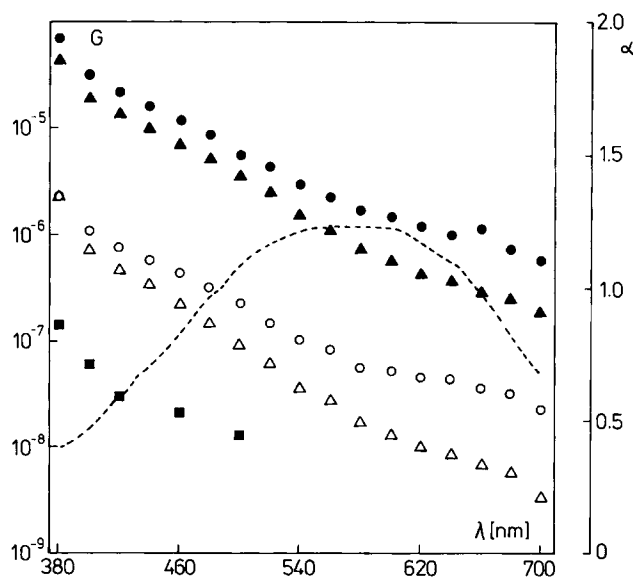


Figure 1 Spectral characteristics of the gain coefficient G [Eq. (1)] of the PDE films: pristine (squares), doped with 4% TCNE (triangles), and with 6% TCNE (circles); open symbols, 10^6 V/m ; full symbols, 10^7 V/m . Broken line shows the absorbance of the sample with 4% TCNE. All measurements were made at the same incident photon flux $4 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$.

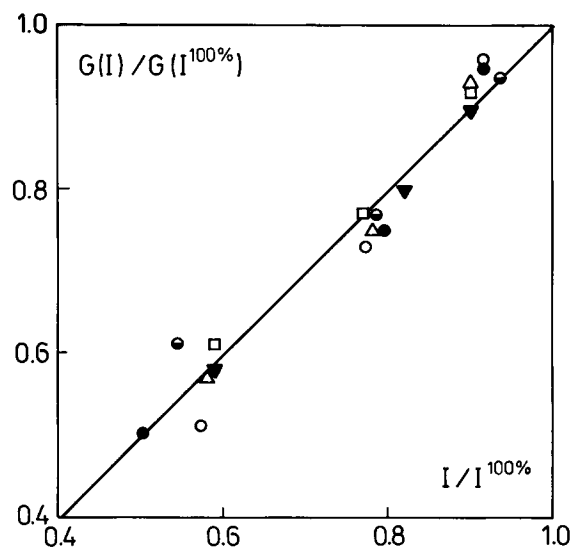


Figure 2 Light-intensity dependence of the photoconductivity illustrated by the dependence of relative gain coefficient on the relative changes of the photon flux.

Sample Symbol	TCNE (wt %)	λ (nm)	$I^{100\%}$ (10^{13} $\text{cm}^{-2} \text{s}^{-1}$)	F (10^6 V/m)
○	4	600	8	1
●	4	500	8	1
●	4	400	8	1
▼	4	400	80	1
△	4	400	80	10
□	6	400	80	1

ternal electric field (10^7 V/m) used in these experiments, the photoconductivity can be observed only for wavelengths shorter than 500 nm.

Dark conductivity for doped samples is greater by more than one order of magnitude than for undoped PDE ($2 \cdot 10^{-18}$ ($\Omega \text{ cm}$) $^{-1}$ for films with 6% TCNE), but the photoconductivity increases more strongly (the gain coefficient for samples containing 6% TCNE increases about 10^3 times; circles in Fig. 1). The increase is remarkable, particularly at longer wavelengths where pure samples do not exhibit detectable photoconductivity. Despite the relatively strong absorption CT band, the photocurrent decreases monotonically with increasing wavelength. However, for the highly doped sample, it is seen that the gain coefficient at larger wavelengths becomes less wavelength-dependent, indicating the presence of another photogeneration mechanism.

In the range of photon flux ($4 \cdot 10^{13} < I < 8 \cdot 10^{14}$ $\text{cm}^{-2} \text{s}^{-1}$) used, the photocurrent is proportional to the light intensity. Such behavior is the same for

different wavelengths, electric fields, and concentrations of TCNE (Fig. 2).

For low fields, the gain coefficient is proportional to the electric field strength F (i.e., the photocurrent is ohmic), but for fields higher than 10^6 V/m, the field dependence becomes stronger and G is proportional to $F^{1.5}$. Such dependence holds for different wavelengths and different TCNE concentrations (Fig. 3). Measurements for fields higher than 10^7 V/m was impossible because of breakdowns. In all the above-discussed experiments, no difference was found for positive and negative polarization of the illuminated electrode.

To compare the properties of PDE with some well-known polymer photoconductor, the analogous measurements of photoconductivity were performed for PVK films. It turned out, however, that contrary to the PDE the photoconductivity effects in the PVK "sandwich" sample are strongly affected by photoinjection from electrodes, e.g., the measured photocurrent depends strongly on the polarization of the illuminated electrode and direct comparison was impossible. A strong photoemission from metal electrodes into PVK was found also by other authors.⁴ For example, for the gold electrode, the action spectrum showed a broad maximum centered around 600 nm, but a steady-state response occurred only with the positive metal electrode. For these reasons, almost all published results concerning spectral de-

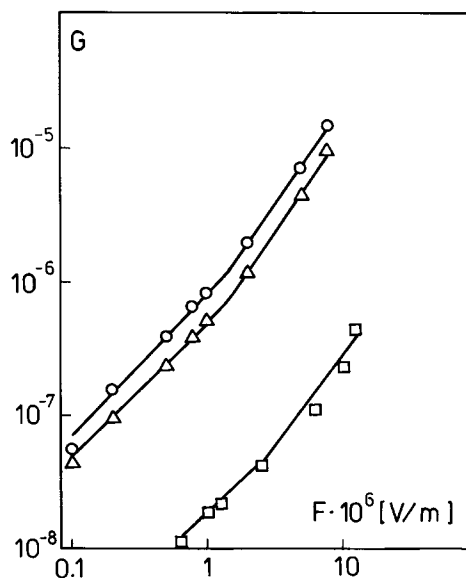


Figure 3 Electric-field dependencies of the gain coefficient at 400 nm for samples with 4% TCNE (triangles) and with 6% TCNE (circles) and at 600 nm for sample with 4% TCNE (squares).

dependencies of photoconductivity in PVK were obtained using the contactless xerographic discharge technique.

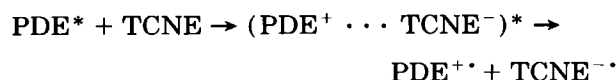
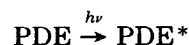
Xerographic discharge tests performed on films without electrodes using Dyntest-90 (limited to low electric fields) have shown that PVK films exhibit in these conditions a higher initial discharge rate than does PDE. One can estimate that the quantum yield (related to the incident light intensity) is ca. 2–3 times higher in PVK films than in PDE doped with 4% TCNE.

DISCUSSION

The measurements of the photoconductivity carried out for pure PDE samples indicate that undoped polymer reveals poor photoconductivity, mainly due to weak absorption in the visible range.

The observed increase of the photoconductivity for the samples sensitized with TCNE is caused by an increase of both charge-carrier mobility and photogeneration. It is consistent with the results of the mobility measurements, which show that after doping with 4% of TCNE the mobility is higher by more than one order of magnitude ($3.6 \cdot 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at the field $4 \cdot 10^7 \text{ V/m}$ as compared to $1.2 \cdot 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for pure PDE at the same field).²

The possible explanation for the spectral characteristic is the existence of two paths for the carrier photogeneration. In the range of wavelengths below 420 nm, the photogeneration is connected to an absorption of the light by the cyclophane unit, formation of the exciplex, and a final exciplex dissociation leading to formation of a mobile charge carrier:



For longer wavelengths, the photogeneration is associated with an absorption by the CT complex and then with a dissociation of the exciplex and formation of a charge carrier:

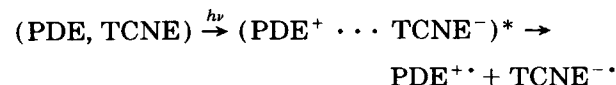


Figure 3 shows that the specific photoconductivity, which is the ratio of the photocurrent density to the electric field, is constant for lower fields but increases proportionally to $F^{0.5}$ for fields higher than 10^6 V/

m. The measurements of the mobility² carried out for samples with 4% TCNE and for fields higher than 10^7 V/m have shown that the mobility is strongly field-dependent; it is approximately proportional to F^2 . This indicates that there is an important contribution of the field dependence of the mobility to the field dependence of the photoconductivity. Therefore, at fields higher than 10^7 V/m , one can expect still stronger field dependence of the photoconductivity. As was explained in the Experimental section, the measurements of the photoconductivity at fields higher than 10^7 V/m were technically difficult because of breakdown. Preliminary xerographic discharge experiments performed using homemade equipment have shown that the discharge rate increases strongly at higher electric field. More detailed studies in the high-field range are necessary in order to compare quantitatively the photoconducting properties of PDE and PVK.

CONCLUSIONS

The pure PDE exhibits poor photoconductivity in the visible range due to low photogeneration yield (weak light absorption) despite relatively high charge-carrier mobility. Doping with TCNE results in a strong increase of the photoconductivity due to an increase of both the mobility and the photogeneration yield. These promising results suggest that using proper sensibilizers (low molecular weight chromophores with acceptor properties) it should be possible to obtain macromolecular materials with photoconductivity comparable or higher than in PVK, but with much better mechanical properties characteristic of the PDE polymer films.

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