POLYPARACYCLOPHANES — POLYMERS WITH π-ELECTRONS DELOCALISED ALONG PENDANT GROUP STACKS

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*Dedicated to Professors Krzysztof Pigoń, Józef W. Rohleder
and Zdzisław Ruziewicz on the occasion of their 70th birthdays**

Recently developed photoconductive polymer systems, polyparacyclo-phanes doped with low-molecular-weight acceptors, combine high charge carrier mobility provided by extended π-electron systems along cofacially arrayed aromatic rings, with effective photogeneration in visible range due to formation of charge-transfer complexes with the dopants. In a series of polyparacyclophane complexed with different benzoquinones it was found that the photoconductivity gain coefficient in the visible range increases with increasing electron affinity of the dopant and that the gain coefficient is higher for higher dopant concentration. The influence of the charge-transfer complex formation between various polyparacyclophanes and various acceptors on the charge carrier generation both in the dark and under illumination is discussed.

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1. Introduction

Photoconductor has to be capable of both photogenerating the charge carriers and transporting them through the bulk. Organic photoconductors have many advantages such as wide spectral sensitivity, low cost and architectural flexibility. The polymeric photoconductors known so far are polymers with saturated backbone containing active chromophores as pendant groups or molecularly dispersed dopants. The poly(*N*-vinyl carbazole) (PVK) sensitized by adding electron

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acceptors like 2,4,7-trinitrofluorenone (TNF) is the best known and widely inves-
tigated polymeric charge-transfer (CT) complex system. The pendant groups and
their CT complexes with acceptor dopants are photogeneration centers. Charge
transport in these materials occurs via hopping among pendant groups and/or
among dopant molecules (at sufficiently high dopant concentration). Due to posi-
tional and energetical disorder in polymeric materials the charge carrier mobility
is usually low, being the main limitation preventing practical application of many
photoconducting polymers on large scale.

It was therefore interesting to investigate new polymers with extended co-
operative electronic effects which are also easily soluble, film forming materials
with good mechanical and optical properties. Poly$((E,E)$-[6.2]paracyclophane-1,5-
-diene) (PDE) is a member of specific polymer group containing bridged rings pen-
dant to the backbone. Relatively rigid polymer chain allows alignment of multiple
cyclophane groups leading to extended π-electron systems [1]. Several groups of
substituted paracyclophane polymers were synthesized being polymeric analogs of
the known stacked arene salts [2]. However, due to polymeric nature of these ma-
terials they have not been prepared as single crystals, and the structure of these
polymers may not allow for a correct arene–arene alignment to achieve maximum
conductivity. The inhomogeneous dispersal of radical cation aligned stacks formed
upon doping throughout the bulk material may also limit the conductivity in the
doped polymers; however the hole mobility found in PDE is high [3]. It is interest-
ing to mention also that they exhibit intense fluorescence arising from alignment
and electronic interactions of multiple repeat units [2].

It has been shown that the charge generation in iodine doped polyparacyclo-
phanes occurs via thermally activated equilibrium, and by decreasing the oxidation
potential of the pendant cyclophane rings the conductivity can be increased [4].
Recently the photoconductivity studies of PDE doped with tetracyanoethylene
(TCNE) have shown a strong increase in the photoconductivity upon doping [5].
These results and the aim to obtain a better insight into these effects lead us
to studies of other low molecular weight (l.m.w.) dopants being chromophores
with acceptor properties. Several benzoquinone derivatives with increasing elec-
tron affinities were used as acceptor additives. It was shown that the photocon-
ductivity of PDE in the visible range is enhanced more by stronger acceptors [6].
The aim of this work is to discuss the influence of the CT complex formation
between polyparacyclophanes and various l.m.w. acceptors on the charge carrier
generation both in the dark and under illumination.

2. Experimental

Poly$((E,E)$-[6.2]paracyclophane-1,5-diene) contains bridged rings pendant
to the polymer backbone (see Fig. 1). PDE films were kindly provided by Prof.
D.T. Glatzhofer (The University of Oklahoma). The films doped with l.m.w. ac-
ceptors were obtained by casting at room temperature under slow evaporation
conditions from dichloromethane solutions. For photoconductivity measurements
semitransparent gold electrodes were evaporated at both sides of the sample. Ref-
erence glass plates were evaporated simultaneously to determine the optical trans-
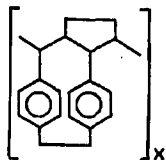mission of the electrodes. The sample, placed in a vacuum chamber with quartz

Fig. 1. Formula of the PDE polymer unit.

windows, 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 and Zonen) thermopile situated in the sample position. Further details of the photoconductivity measurements were published elsewhere [5, 6]. Spectral response characteristics were obtained by keeping the photon flux constant, equal to 4×10^{13} cm^{-2} s^{-1}. The results were expressed by the effective gain coefficient G

$$G = (j_{\mathrm{ph}} - j_{\mathrm{d}})/e(1 - T)N_0, \tag{1}$$

where j_{ph} is the photocurrent density, j_{d} — the dark current density, T — the transmission of the doped polymer film and N_0 is the incident photon flux corrected for absorption of the electrode.

Four benzoquinone derivatives were chosen as acceptors with increasing electron affinities: p-benzoquinone (quinone), tetra-methyl-p-benzoquinone (duroquinone), tetrachloro-p-benzoquinone (chloranil) and 2,3-dichloro-5,6-dicyano-p--benzoquinone (DDQ). Molar concentration of all these dopants was constant, yielding approximately one dopant molecule per 13 cyclophane units, the same as in the previously studied system PDE + 4 wt.% TCNE [5]; it means that the wt.% concentrations were different.

3. Results and discussion

The different electron affinities (EA) of the used acceptor dopants: (a) quinone ($EA = 0.4$ eV), (b) duroquinone ($EA = 1$ eV), (c) chloranil ($EA = 1.37$ eV), (d) DDQ ($EA = 1.9$ eV) (Ref. [7], p. 386) at constant molar concentration in the PDE films under study result in different shifts of spectral sensitivity expressed by the gain coefficient G as it was shown in [6]. For higher EA values the photoconductivity action spectra are more extended into visible range. The gain coefficient G as a function of the EA of the investigated benzoquinones dopants (log G vs. EA plot) at constant molar concentration and at wavelength 500 nm is shown in Fig. 2. One should note that the gain coefficient G is normalized in respect of the transmission of the samples, therefore an increase in G with increasing electron affinities of the acceptor dopants is not due to an increasing absorption of the films. In fact, as one can see in Fig. 3, the transmission of the investigated films at 500 nm does not increase monotonously with increasing electron affinity of the dopants.

It was also found that the gain coefficient G depends on the acceptor dopant concentration, as illustrated for the PDE + DDQ system in Fig. 4. The chosen wavelength, 500 nm, corresponds to the CT band of the PDE/DDQ complex. According to the definition given by Eq. (1) the gain coefficient G is the ratio of
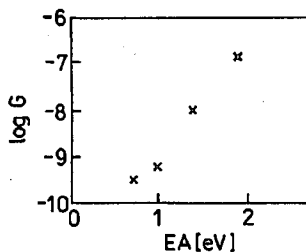
J. Ulański, M. Kryszewski

Fig. 2.   Dependence of the photoconductivity gain coefficient G on the electron affinity *EA* of the additives for PDE doped with various benzoquinones. Molar concentration of dopants is constant. $F = 5 \times 10^6$ V/m, wavelength = 500 nm.
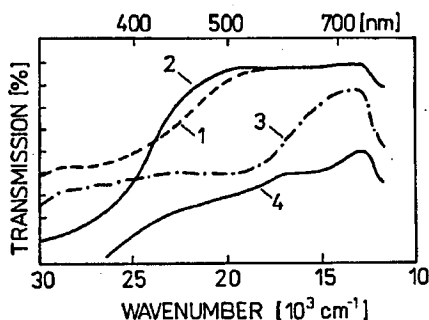

Fig. 3.   Transmission spectra of the PDE films doped with: 3.2 wt.% of quinone (curve 1), 4.8 wt.% of duroquinone (curve 2), 7 wt.% of chloranil (curve 3) and 6.7 wt.% of DDQ (curve 4).
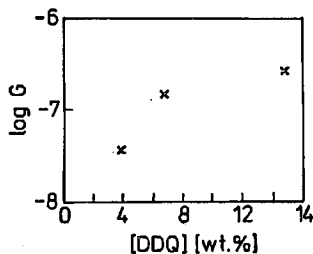

Fig. 4.   Dependence of the photoconductivity gain coefficient G on the DDQ concentration in PDE. $F = 5 \times 10^6$ V/m, wavelength = 500 nm.

the number of the photogenerated charge carriers collected by the electrode per time unit to the photon flux effectively absorbed by the polymer film. Therefore one can expect that G should be independent of the film absorption for low dopant concentration, unless the dopant molecules affect not only the photogeneration but also the charge carrier transport.

The dependence of G on the DDQ concentration shown in Fig. 4 can be

rationalized taking into account that upon complexation the benzene rings in cyclophane units become more nearly parallel leading to an increasing charge carrier delocalization as it was shown for l.m.w. paracyclophanes and its CT complexes (Ref. [7], p. 288). This may result not only in the previously found increase in the charge carrier mobility in PDE upon complexation [3], but also in an enhancement of photogeneration efficiency, because the charge carrier dissociation can be promoted by the increased average electron–hole separation.

The role played by the CT complexation in the charge carrier generation was demonstrated independently for the series of polyparacyclophanes containing benzene, *p*-dimethoxybenzene or thiophene moieties in the pendant groups complexed with iodine [4]. It was found that the dark conductivity increases and the activation energy of conductivity decreases with decreasing oxidation potential of the cyclophane repeat units. This is consistent with a weaker thermally activated generation of charges for stronger complex formation.

4. Conclusions

CT complexes of polyparacyclophanes with l.m.w. acceptors are heterogeneous materials on molecular level. In such systems the charge carrier localization is usually associated with domain-like suborganization (for review of charge transport in heterogeneous materials see e.g. [8]), but due to delocalization along stacked pendant groups, the cyclophane groups are not the localized states, in contrast to e.g. carbazole pendant groups in PVK.

The increase in the number of charge carriers generated in the polyparacyclophane systems can be realized by increasing the electron affinity of the dopant molecules and/or by decreasing the oxidation potential of the pendant cyclophane groups.

Acknowledgment

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