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Mechanisms of Doping and Spectral Sensitization of Polymer Photoconductors, Especially Poly-N-Vinylcarbazole

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Summary: Photoconductivity of organic polymers can be greatly enhanced and extended into the visible region by the addition of small amounts of additives, such as electron acceptors and dyes. These effects can be explained as the result of photoredox processes and as the result of an influence of local fields of donor-acceptor complexes upon the photogeneration of charge carriers.

1. Introduction

There is an increasing interest in using organic photoconductors for studying scientific questions and for an application, among others, in the field of electrophotography (SCHAFFERT 1971, BALTAZZI 1981) or in photoelectrodes capable of the dissociation of water by utilizing solar energy (MEIER et al. 1979). However, photoelectric sensitivity of organic materials may be restricted up to now by inhibitions of synthesizable structures (MEIER 1974). Therefore, the possibility of an improvement of photoconductivity of organic solids, especially polymers, by the addition of dopant molecules is very important.

In this paper some remarks about the mechanisms of doping with electron acceptors and dyes are given. Results are restricted above all to poly-N-vinylcarbazole (PVCA) which is used in electrophotographic imaging processes (REUCROFT and TAKAHASHI 1977, TERRELL and KILLAT 1980, WEIGL 1977, LUEBBE and MALTZ 1980).

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2. Experimental

PVCA without any binder was prepared by dipping metal-coated glass slides into the carbazole solution, or by pouring the solution onto plates and removing the solvent by evaporation. Dopants and dyes, respectively, were added to the solution before preparation. The acceptors used as dopants were iodine, tetracyanoethylene (TCNE), tetracyanochinodimethane (TCNQ) and o-chloranil (o-CA).

For the electrical measurements, among others, the vidicon arrangement which is also used in television pickup tubes (MEIER and ALBRECHT 1969, MEIER 1976) and the time-of-flight technique (KEPLER 1960, MEIER et al. 1976) was employed. The fluorescence emission of PVCA was measured with a Perkin Elmer 650-10 S fluorescence spectrophotometer.

3. Results and discussion

In discussing the influence of dopant molecules various types of doping on photoconductivity of polymers should be distinguished: Impurity doping, photosensitization with dyes, acceptor (donor) doping and acceptor/dye doping (i.e., supersensitization). Concerning these different types of doping the following facts and mechanisms can be pointed out.

3.1. Impurity doping

Impurity doping is characterized by a reduction of the photoconductivity of organic materials by the incorporation of small amounts of specific compounds. This effect may often be ascribed to a reduction of the mobility of free charge carriers as a result of multiple trapping as proven by photocurrent transients (ITOH et al. 1973). The reason is that foreign molecules can act

- as hole traps if their ionisation energy is smaller than the ionisation energy of the host or
- as electron traps if their electron affinity is greater than

the electron affinity of the host material.

With this mechanism valuable hints at the influence of impurities, additives (e.g., antioxidant agents) or disturbances of the polymer chain can be obtained which point to hole of electron trapping in polymers (BAUSER 1972). For instance, the observation of a decrease of photosensitivity of dye-sensitized PVCA beyond a certain concentration of the dye (e.g., malachite green as discussed by MORT and PFISTER (1979)) may be ascribed to trapping of mobile holes by the dye in its groundstate. Moreover, 0.56 eV traps observed by KITAYAMA et al. (1980) with UV light-thermally stimulated currents may be formed, among others, by photooxydation products of PVCA acting as electron acceptors as suggested by PFISTER and WILLIAMS (1974).

3.2. Photosensitization with dyes

The photoresponse of PVCA and other polymeric photoconductors can be extended to the visible region by the addition of dyes (in the form of solutions, dispersions or thin compact layers as reviewed by ROCHLITZ (1976)) belonging to different classes; see, e.g., MEIER et al. (1972) and PENWELL et al. (1978). In discussing the mechanism of spectral sensitization it should be notized, among others,

- that the wavelength dependence of sensitized photoconductivity corresponds to the absorption spectrum of the dye
- that the sensitization efficiency increases by using dyes with increasing electron affinities (MINEGISHI et al. 1974)
- that the efficiency of dye sensitization may depend upon the concentration of donor sites which may be formed, e.g., in PVCA, by monomer units or in carbazol-substituted thermoplastic PVCA by methacrylate or styrene units (TERRELL 1977).

These experimental results point to a redox mechanism according to which in the primary excitation process an electron is transferred between the excited dye molecule and a polymer chromophor or donor site. Therefore, relative redox-potentials of the excited dyes and the unexcited donor units of polymers are important in the photosensitization step which produces free carriers. Moreover, competitive processes, either radiative or nonradiative in nature (MORT and PFISTER 1979), and the trap character of unexcited dyes must be taken into account.

As an example of photosensitization, in figure 1, curve 1 shows the extension of the photocurrent of PVCA into the visible range by the addition of methylene blue.

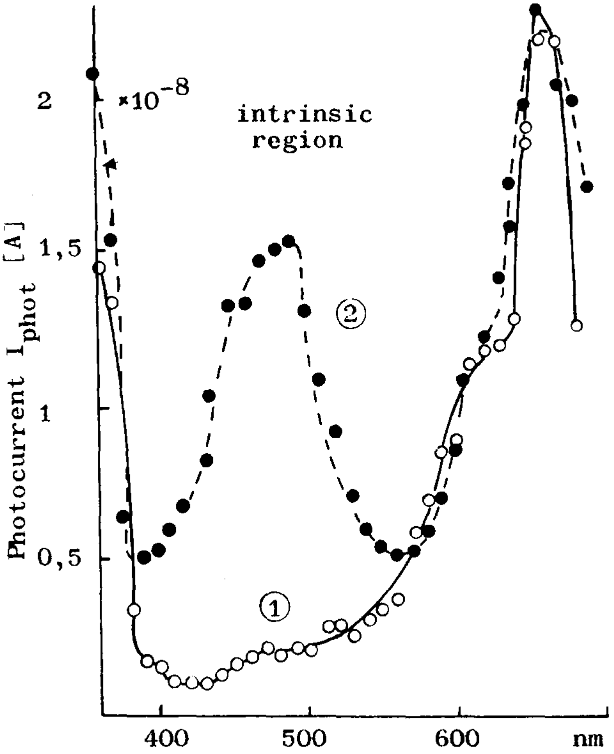

Fig. 1 Action spectrum of photoconductivity of PVCA

① PVCA + methylene blue

② PVCA + methylene blue + TCNE

Sandwich-type cell: Vidicon arrangement.

3.3. Acceptor (donor) doping

Doping of photoconductivity of PVCA with electron acceptors first oberved by HOEGL et al. (1972) is characterized, among others, by the following facts:

1. Photoconductivity of PVCA can be increased remarkably by the incorporation of small amounts of electron acceptors such as iodine, o-CA, TCNE or TCNQ.

2. Analogous to dark conductivity, photoconductivity increases with the concentration of the dopant (according to $\sigma_{Ph} = a \cdot c^{\beta}$ with $\beta = 2.4$ in PVCA/o-CA).

3. Between electron affinities of acceptors and their ability for doping because of steric effects no clear correlation exists.

Acceptor doping cannot be considered as the result of the influence of dopants upon the transport of holes as shown by MEIER et al. (1969). Moreover, it is difficult to postulate any change of the recombination paths for charge carriers in doped PVCA. Therefore, doping may be connected with the photogeneration step. That means, the efficiency of photogeneration will be increased by the formation of carriers as a result of charge-transfer band excitation (a) or as a result of the formation of exciplexes (b) and excitons, respectively (MEIER et al. 1981):

(a) With regard to the charge-transfer mechanism it is remarkable that the CT-band which is situated at 600 nm in PVCA-films cannot be observed in the photoconduction spectrum.

(b) The doping effect results from an enhancement of the intrinsic photoconductivity of the polymer (see figure 2), an observation which would be in agreement with an exciplex mechanism. However, the degree of fluorescence quenching observed in PVCA by the addition of acceptors deviates from their ability for doping photoconductivity: Fluorescence quenching is in the order I_2 < o-CA < TCNQ and the enhancement of photoconductivity follows the order TCNQ < TCNE < o-CA < I_2. This observation is contrary to the expectation that the quenching of

PVCA fluorescence by acceptors should go parallel with the ability of the dopants in increasing the charge carrier photogeneration efficiency (LOUTFY and MENZEL 1980).

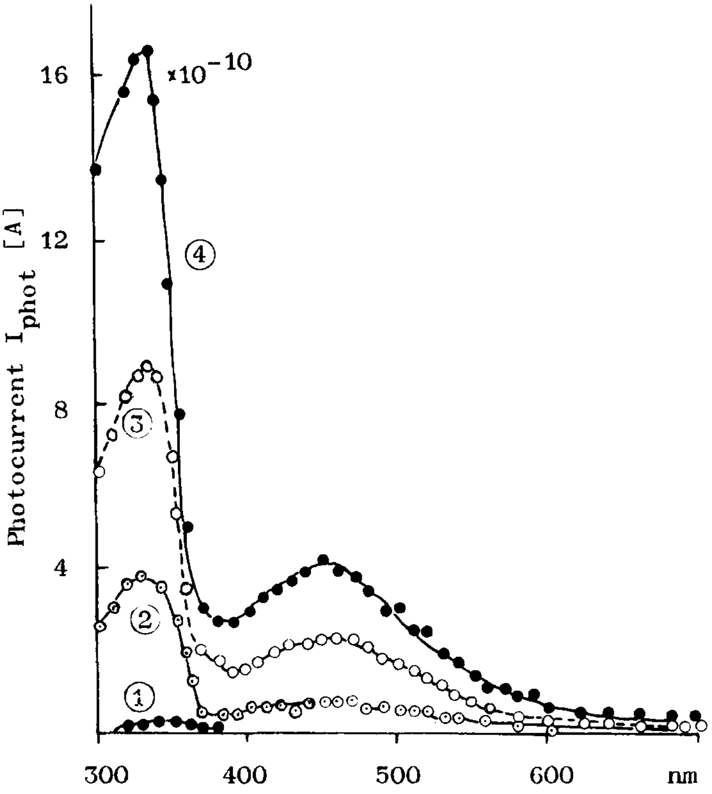

Fig. 2 Action spectrum of photoconductivity of PVCA Sandwich-type cell (illuminated electrode: positive)

① PVCA (purified): without any dopant

② o-chloranil/PVCA (monomer) = 1.44 × 10^{-2}

③ o-chloranil/PVCA (monomer) = 2.16 × 10^{-2}

④ o-chloranil/PVCA (monomer) = 2.88 × 10^{-2}

Because of these difficulties in explaining doping effects in PVCA we think that a combined mechanism should be discussed resulting from:

- Charge-transfer complex formation of PVCA/Acceptor pairs in the ground state.

- Dissociation of diffusing excitons (RIPPEN and KLÖPFFER 1979) into free carriers within local fields (MUNN 1981) formed by electrical dipols of ground-state charge-transfer complexes.

With this mechanism, among others, the correlation between fluorescence quenching and increase in charge carrier photogeneration efficiency is understandable. However, further measurements are necessary for a quantitative recording.

3.4. Acceptor/Dye doping (Supersensitization)

With combinations of acceptor dopants and small amounts of dyes we could not only obtain an increase of photoelectric sensitivity, but the spectral region of the photoconductive response of PVCA could also be extended from its intrinsic range into the visible region (MEIER et al. 1972). This increase can mainly be ascribed to the formation of an additional peak in the action spectrum of photoconductivity lying between the polymer- and dye-peak, as shown in figure 1. Moreover, the intensity of the additional peak depends on the concentration of the dye. Furthermore, the position of this peak depends on the kind of the added acceptor: with TCNE the peak lies at about 490 nm and with TCNQ at about 410 nm.

Supersensitization may be explained by the transfer of electrons between excited acceptor radical anions of the charge-transfer complexes and dye molecules in their ground-states. This results in a reduced dye and an oxidized acceptor radical. Whereas the reduced dye probably injects an electron into a conducting state of PVCA the acceptor can be reduced by a thermally induced electron transfer from the polymer so that, in addition, a hole might be generated. A change of hole and electron concentration observed in photocurrent transients is in agreement with this mechanism.

4. Literature references

BALTAZZI, E.S.: Chem. Ind. (London) 34 (1981)
BAUSER, H.: Kunststoffe 62, 192 (1972)
HOEGL, H., BARCHIETTO, G. and TAR, D.: Photochem. Photobiol.

16, 335 (1972)
ITOH, U., TAKEISHI, K. and ANZAI, H.: J. Phys. Soc. Jap. 35, 810 (1973)
KEPLER, R.G.: Phys. Rev. 119, 1226 (1960)
LOUTFY, R.O. and MENZEL, E.R.: J. Amer. Chem. Soc. 102, 4967 (1980)
LUEBBE, R. and MALTZ, M.: Photogr. Sci. Eng. 24, 205 (1980)
MEIER, H. and ALBRECHT, W.: Ber. Bunsenges. Phys. Chem. 73, 86 (1969)
MEIER, H., ALBRECHT, W. and TSCHIRWITZ, U.: Ber. Bunsenges. Phys. Chem. 73, 795 (1969)
MEIER, H., ALBRECHT, W. and TSCHIRWITZ, U.: Current Problems in Electrophotography (W.F. BERG and K. HAUFFE, eds.) W. de Gruyter, Berlin, 1972, pp. 163
MEIER, H., ALBRECHT, W. and TSCHIRWITZ, U.: Photochem. Photobiol. 16, 353 (1972)
MEIER, H.: "Organic Semiconductors: Dark- and Photoconductivity of Organic Solids", Verlag Chemie, Weinheim 1974
MEIER, H., ALBRECHT, W. and TSCHIRWITZ, U.: Photogr. Sci. Eng. 20, 72 (1976)
MEIER, H.: Topics Current Chem. 61, 85 (1976)
MEIER, H., ALBRECHT, W., TSCHIRWITZ, U., GEHEEB, N. and ZIMMERHACKL, E.: Chem.-Ing. Tech. 51, 653 (1979)
MEIER, H., ALBRECHT, W., TSCHIRWITZ, U. and GEHEEB, N.: Materials Science VII, No. 2-3, 259 (1981)
MINEGISHI, T., KONDO, E., YAMANOUCHI, T. and KINJO, K.: Z. phys. Chem. 91, 13 (1974)
MORT, J. and PFISTER, G.: Polym.-Plast. Technol. Eng. 12 (2), 89 (1979)
MUNN, R.W.: Materials Science VII, No. 1, 62 (1981)
PENWELL, R.C., GANGULY, B.N. and SMITH, T.W.: J. Polym. Sci.: Macromol. Rev. 13, 63 (1978)
PFISTER, G. and WILLIAMS, D.J.: J. Chem. Phys. 61, 2416 (1974)
REUCROFT, P.J. and TAKAHASHI, K.: Thin Solid Films 46, 321 (1977)
ROCHLITZ, J.: Chem. Ztg. 100, 351 (1976)
RIPPEN, G. and KLÖPFFER, W.: Ber. Bunsenges. Phys. Chem. 83, 437 (1979)
SCHAFFERT, R.M.: IBM J. Res. Dev. 15, 75 (1971)
TERRELL, D.R.: Photogr. Sci. Eng. 21, 66 (1977)
TERRELL, D.R. and KILLAT, U.: Photogr. Sci. Eng. 24, 25 (1980)
WEIGL, J.W.: Angew. Chem. Int. Ed. 16, 374 (1977)

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