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Intramolecular Charge Transfer Complexes

22. Photoconductivity of Donor-Acceptor Copolymers in Thin Samples

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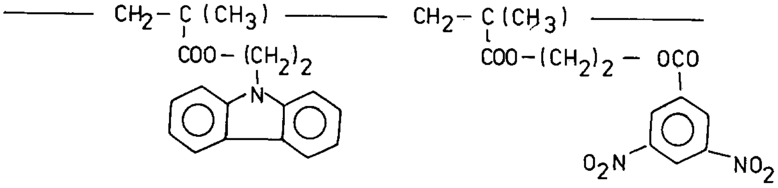
SUMMARY

The dependence of the photoconductivity on the composition of copolymers with pendant electron donor and acceptor groups is presented for the case of film samples. Such a dependence shows a relative maximum when the irradiation level is low and an absolute maximum when the irradiation level is high enough. The maxima position corresponds roughly to the 1:1 copolymer composition . This dependence was explained for the case of positive illuminated electrode potential by supposing a logarithmic decreases for the hole mobility,and a Gaussian dependence for the probability of donor group photoionization.

INTRODUCTION

The visible range photoconductivity measured on thick samples (pellets) for the HECM-DNBM copolymer was presented as a function of composition (1). A characteristic of the HECM-DNBM copolymer is that it contains both the electron donor (D) and the electron acceptor (A) groups as pendant substituents. For this reason this copolymer,as well as other copolymers synthesized by us,shows charge transfer complex properties,e.g.photoconductivity (2).

The present paper is concerned with photoconductivity measurements on thin and rather uniform films,considering that film samples are more suitable than thick samples to interpret the measured conductivity as photoconductivity. The study was also performed on HECM-DNBM copolymer having the molecular structure:



HECM (D) DNBM (A)

EXPERIMENTAL

HECM-DNBM copolymers of various compositions (seven values) were prepared according to the method described elsewhere(3).

Film samples were obtained on SnO2 covered glass plates from nitrobenzene solutions as follows:

Solutions of 5% polymer concentration were prepared from the HECM-DNBM copolymers of various compositions,and from the parent homopolymers (polyHECM,polyDNBM). The glass plates were horizontally placed on a heater at about 30°C. A film sample was obtained by laying 0.1 ml well filtered solution to get a circular spot of about 5 cm^2. The temperature was then slowly increased at 120-130°C,kept at this value for 2 hours,and then slowly decreased at 30°C. The samples were covered (not hermetically) durring heating to maintain a solvent vapour atmosphere. The check of solvent removing was made by IR spectroscopy. The film thus prepared had a 8-11µm thickness in a central area of 16 mm diameter.

The attempts made with volatile solvents as tetrahydrofuran and dioxane led to worse films (ununiforme and/or cracked),perhaps due to a too rapid evaporation or a low solubility.

The photoconductivity measurements were carried out under vacuum at room temperature by using a cell previously described (1). The electrode on the unilluminated surface has a diameter of 16 mm and is covered with electric conducting rubber. It was observed that the films show some microcracks, the width of which being smaller than 1 µm. For this reason, electrodes deposed by metal evaporation were not used.

The measuring cell was connected to an electrometer of Teralin III Straton type. The voltage applied across the film samples was of 1 Vcc,the breakdown tendency being observed at more than 5-10 V. The meaurements were carried out for the both polarities: A-when the illuminated electrode potential was positive, and B-when the same potential was negative.

The illumination of samples was made by means of a LOS-1M irradiater equipped with a Xenon lamp. The irradiation level was changed by means of the slit between the lamp and the condenser.

The irradiation was made in visible range,the ultraviolet radiation being strongly attenuated by the glass support of films.

RESULTS AND DISCUSSION

1. Photoconductivity as a function of copolymer composition for A polarity

The photoconductivity dependence on HECM-DNBM copolymer composition is given for three different irradiation levels in Figure 1A. One can observe that:

a) For low irradiation levels (curves IA and IIA) the photoconductivity decreases when the content of electron acceptor (donor) unit increases (decreases),but shows a weak relative maximum for values smaller than 50% DNBM.

b) For high irradiation levels (curve IIIA) the photoconductivity shows an evident absolute maximum for about 1:1 copolymer composition.

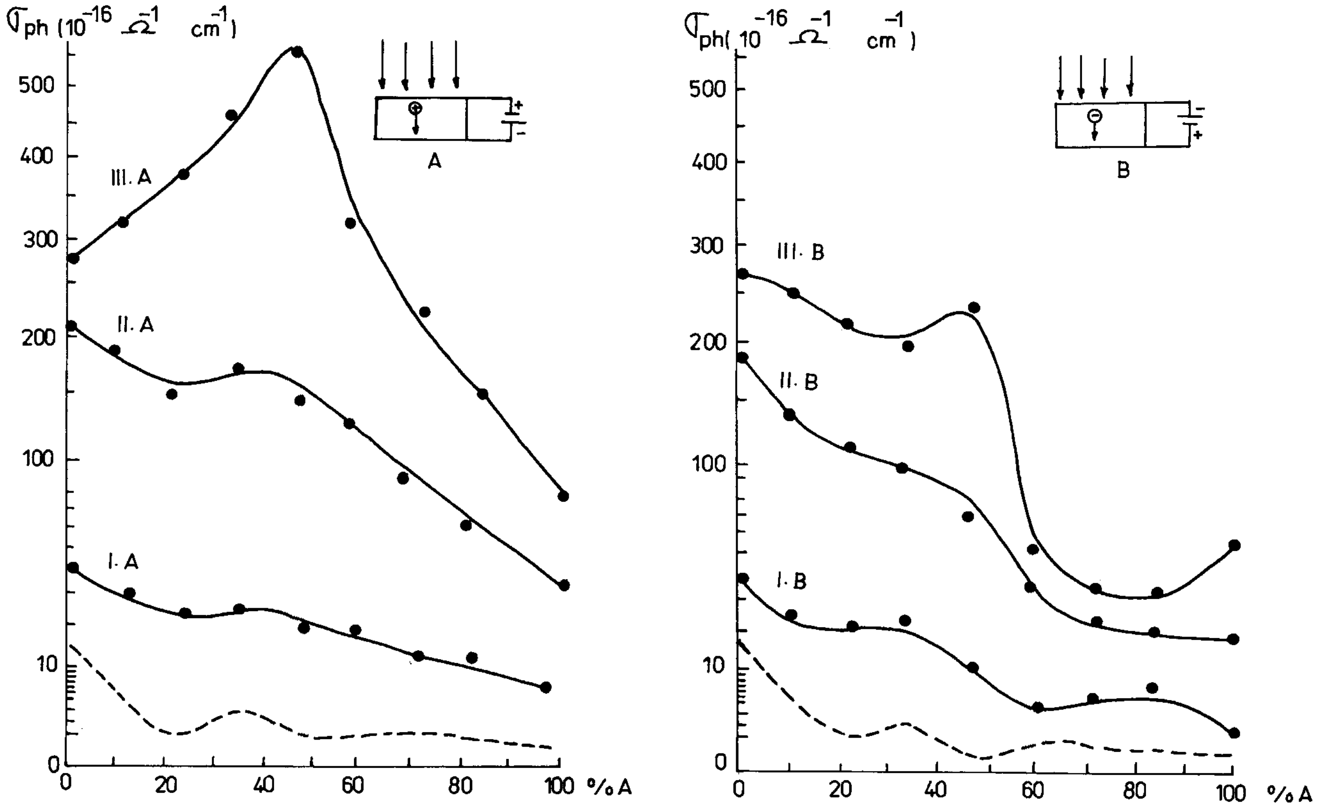


Figure 1-Photoconductivity against composition for thin samples of the HECM-DNBM copolymer. The curves A and B are different one another by the polarity of voltage across the sample,and are given for three xenon illumination levels: 7 mW/cm^2 (I),50 mW/cm^2(II) and 500 mW/cm^2(III).The dashed curves correspond to the photoconductivity of thick samples (400 µm, 20 mW/cm^2) (reference 1).

Tentative explanation

When the illuminated electrode potential is positive, the electric field inside the copolymer film favours the electric conduction by holes(4)Because the density of photogenerated electron-hole pairs is maximum near the illuminated surface, the electric current inside the sample is due to hole drift to the negative electrode (Figure 2A). In such condition it is expected hole mobility (μ^+) to decrease when the concentration of electron donor groups (D=HECM) decreases, or the concentration of electron acceptor groups (A=DNBM) increases, because hole conductivity is maximum on channels of the type:

$$\underline{\text{Light}}\rightarrow \quad + \quad | \; \overset{\oplus\longrightarrow}{D\;e}\; D \quad D \quad D \cdots\cdot D \; | -$$

and the electron acceptor groups cause the interruption of such conduction ways (Figure 2B).

On the other hand, the photoionization of electron donor groups is easier for charge transfer complex states, and the maximum density of such states is expected to correspond to the copolymer of 1:1 composition. It results that the dependence of the photoholes density (p^*) on the composition of a copolymer with pendant electron donor and acceptor groups can be aproximated by the curve given in Figure 2B.

Supposing that the curves in Figure 2B are generated by the functions:

$$\mu^+ = \mu_0^+ \exp(-ax) \qquad \text{and}$$

$$p^* = p_0^* \exp[-b(x-0.5)^2] \qquad (1)$$

where x is the fraction of electron acceptor units in copolymer, and a, b are positive parameters, the following equation for hole photoconductivity results:

$$\sigma^+_{ph} = \sigma^+_{ph,0} \exp[-bx^2-(a-b)x-0.25b] \quad (2)$$

where $\sigma^+_{ph,0} = e.\mu_0^+.p_0^*$

According to equation (2), the maximum photoconductivity should have the following coordinates:

$$\sigma^+_{ph,M} = \sigma^+_{ph,0} \exp(a^2/4b - a/2) \text{ and } x_M = 0.5-0.5a/b \quad (3)$$

The following observations can be made:

- When $b < 2a$, the dependence $\sigma^+_{ph}(x)$ is of the type of that given in Figure 2C, therefore corresponds to curves IA and IIA in Figure 1A. Its maximum is lower than $\sigma^+_{ph}(o)$ and placed at $0.25 > x_M$.
- When $b > 2a$, the dependence $\sigma^+_{ph}(x)$ is of the type of that also given in Figure 2C, therefore corresponds to the IIIA curve in Figure 1A. Its maximum is higher than $\sigma^+_{ph}(o)$ and placed at $0.25 < x < 0.5$.
- When $b >> a$, it results:

$$\sigma^+_{ph,M} = \sigma^+_{ph,0} \exp(-a/2) \text{ and } x_M \simeq 0.5 \qquad (4)$$

It was found that the IIIA curve in Figure 1A corresponds well to the following parameters: $a = 1 \div 1.5$ and $b = 5 \div 6$.

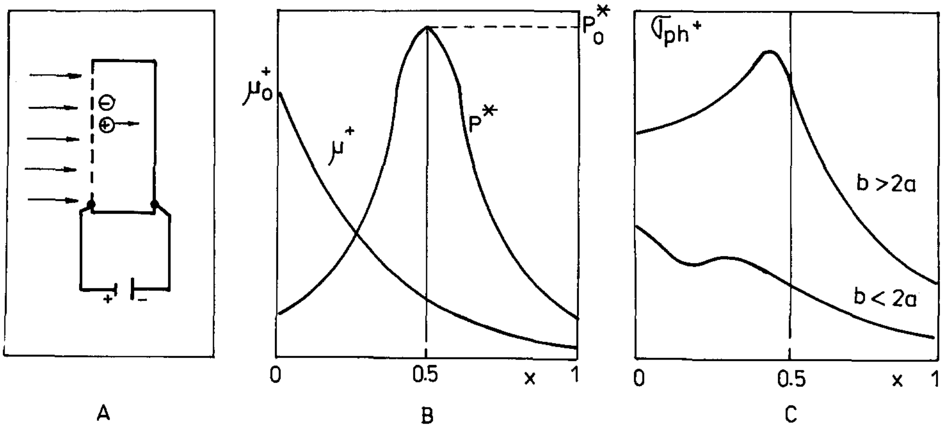


Figure 2- An explanation for hole photoconductivity for thin samples of a copolymer with pendant donor and acceptor groups: A-the electric current inside the sample for A polarity, B-copolymer composition dependences supposed for the drift hole mobility (μ^+) and for the photoholes density (p^*),and C-the hole photoconductivity for the cases $b < 2a$ and $b > 2a$.

The equation (2) supposed for hole photoconductivity is expected to reproduce correctly the dependence on copolymer composition when:

-the density of photoexcited states is much lower than the density of steady states,so that the hole mobility is not dependent on the irradiation level,and

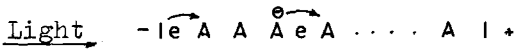
-the photoexcited states are uniformly distributed inside the sample.

Such conditions can be realized by using low enough irradiation powers and samples with thickness much smaller than the reversal of the radiation absorption coefficient. The absorption of the studied copolymers in the visible range is maximum at about λ = 400 nm and the absorption coefficient values increases from 0.02 to 0.08 μm^{-1} when the acceptor unit content increases.That means that sample thickness of about 10 μm (as used) seems to be too big only for the samples of high acceptor unit content.

2.Photoconductivity as a function of copolymer composition for B polarity

This dependence is also given for three different irradiation levels in Figure 1B. The main difference between curves A and B is that the second one shows weak relative maxima even at high irradiation levels.

Considering that B polarity favours the photoconduction by electrons and electron conduction channels are of the following type:



it is surprinsing that the photoconductivity decreases with the increase of electron acceptor unit content. However, such a behaviour might be explained if:

- the photocarriers appear mainly by the photoionization of electron donor groups
- the affinity for electrons of the ionizated donor groups (D^+) is higher than that of the neutral acceptor groups, and
- the photocarriers are due to the photoionization of electron acceptor groups if donor group content is very low.

Anyway, the resemblance between curves A and B obtained at low irradiation levels is still difficult to be explained. For uniforme radiation fields inside the sample, no differences should be observed between these curves, because the ionizated group density should be also uniforme in such a case. Eventual differences should be determined in this case by the differences between the mobilities of holes and electrons.

CONCLUSIONS

The photoconductivity in film samples of a copolymer with pendant electron donor and electron acceptor groups tends to have a maximum for the 1:1 composition. This tendency is evident when the illuminated electrode potential is positive and the irradiation level is high enough.

The photoconductivity dependence on copolymer composition can be well explained for positive illuminated electrode potential, by a logarithmic decrease of the hole mobility and a Gaussian (and perhaps Lorentzian) dependence (with the maximum at the 1:1 composition) of the probability of donor group photoionizations.

The same photoconductivity dependence is still difficult to be explained for negative illuminated electrode potential.

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