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Intramolecular Charge Transfer Complexes

21. Photoconductivity in N(2-Hydroxyethyl) Carbazolyl Methacrylate-Methacryloyl-β-Hydroxyethyl-3,5-Dinitrobenzoate Copolymers

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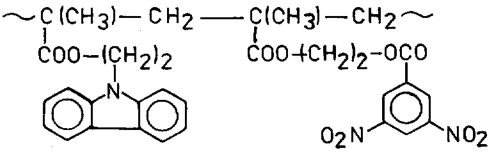
SUMMARY

The photoconductivity was studied on donor-acceptor copolymers of various compositions. The measurements were carried out on pellet samples in which the charge carriers were continuously injected by a shallow illumination with a xenon lamp. It was found that the photoconductivity decreases with the acceptor unit content increase, two relative maxima being however evidenced at 25-35 % and 60-70 % respectively. It was supposed that the two maxima are due to the dependence of the drift mobility on the copolymer composition. It was observed that the polarity of voltage applied across the samples has a minor effect on the conductivity measurements.

INTRODUCTION

The copolymers of poly(donor-co-acceptor) type described in previous papers (SIMIONESCU et al. 1980,1981 ; PERCEC et al. 1981 ; NATANSOHN 1983) show some properties characteristic to the charge transfer complexes, as follows: - a solubility lower than that of the corresponding homopolymers, - a colouring, while the homopolymers are colourless, - a shifting of NMR signals depending on composition, and - an evident crystallization tendency. Actually, they are rather weak complexes because, for example, the absorption in visible range follows quite well the Lambert-Beer law, and the electrical conductivity is very low (10^{-16} - 10^{-17} $\Omega^{-1} \cdot cm^{-1}$). Nevertheless, the poly(donor-co-acceptor) systems differ from the common insulating polymers by evident photoconductivity properties, and it is the purpose of this paper to present some results obtained on the N-(2-hydroxyethyl) carbazolyl mathacrylate (HECM) - methacryloyl- β -hydroxyethyl-3.5-dinitrobenzoate (DNBM) copolymers of various compositions.



HECM DNBM

A structural feature of such copolymers is that the complexation interactions lead to an arrangement where the surfaces of donor (carbazole,in this case) and acceptor (dinitrobenzoate,in this case) groups become parallel each other. Such an arrangement can be evidenced by the composition dependence of the proton NMR chemical shifts (NATANSOHN 1983). More,if the interactions between comonomers are considered,one has to expect that the sequence distribution and the tacticity present a certain degree of ordering.

EXPERIMENTAL

The copolymers were synthesized in dioxane according to a method previously described (PERCEC et al. 1981b),and their compositions were determined by means of proton NMR spectra obtained in dioxane at 90°C.

The electrical conductivity measurements were performed on pellet samples,the crystallization tendency making impossible the obtaining of uniform films. To interpret the experimental results,the copolymer pellets were obtained in similar conditions,namely: drying of copolymers by heating in vacuum at 80°C for one hour,compression under vacuum at 10 tf, the diameter of pellets being of 16 mm and the thickness of 0.41 ± 0.02 mm, and keeping the samples under vacuum until the measurement time. The measurements were carried out under vacuum,at room temperature,by using the cell presented on the Figure 1 and an electrometer of Teralin III Statron type with a sensitivity better than $5 \cdot 10^{-14}$ A. The electrical resistivity was found to increase directly proportional to the pellet thickness,so that the contribution of surface currents was negligible. The voltage applied across the sample was of 300 Vcc and the measurements were carried out for the both polarities.

The illumination of samples was made according to Dember's technique (PEARSON et al. 1979). The radiation source was a xenon lamp and the irradiation power was of 18 - 20 mW/cm^2. The dark (σ_d) and illumination conductivities (σ_{ph}) were determined according to the procedure in the Figure 2.

Specification concerning the illumination effect on the conductivity. The photogeneration of charge carriers takes place in a shallow layer because the samples are quite thick and not transparent. In such conditions,the conductivity at illumination or photoconductivity σ_{ph} (as it will be denoted further) is actually a dark conductivity increased by a carrier photoinjection. So,the photoconductivity σ_{ph} has the following expression:

$$\sigma_{ph} = \sigma_t - \sigma_d = e.n.\mu$$

where μ is the drift carrier mobility and n the photocarrier density into the shallow layer (MORT,1980). The mobility depends only on the sample,while the carrier density depends on both the sample and the illumination characteristics (power and spectral distribution). To separate the two contributions,the photoconductivity was also measured on the samples plated with a very thin selenium layer,so that the photoinjected carrier contribution was the same for all samples,therefore not dependent on copolymer composition.

This photoconductivity was denoted by $^*\sigma_{ph}$ and its characteristic curves (Figure 3) represent the dependence of the mobility μ on the copolymer composition. As it is observed, the photoconductivity $^*\sigma_{ph}$ is a little lower than the photoconductivity σ_{ph} ,this indicating that the photogeneration efficiency of selenium is lower than that of carbazole group, perhaps due to the light reflection. The selenium layer was obtained by thermal evaporation in high vacuum.

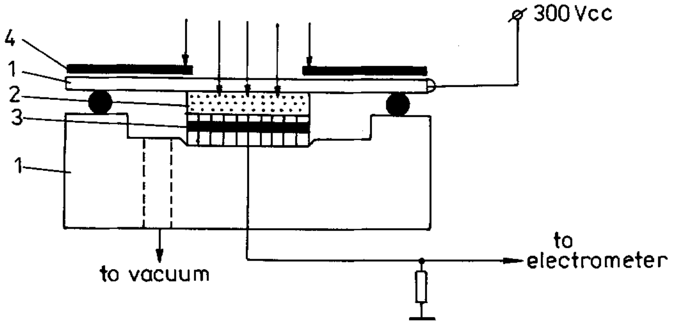


Figure 1. The measuring cell : 1 - glass electrode plated with SnO_2, 2 - copolymer pellet, 3 - flexible electrode composed of two regions of conducting rubber and one of metal, 4 - mask, and 5 - teflon mantle.

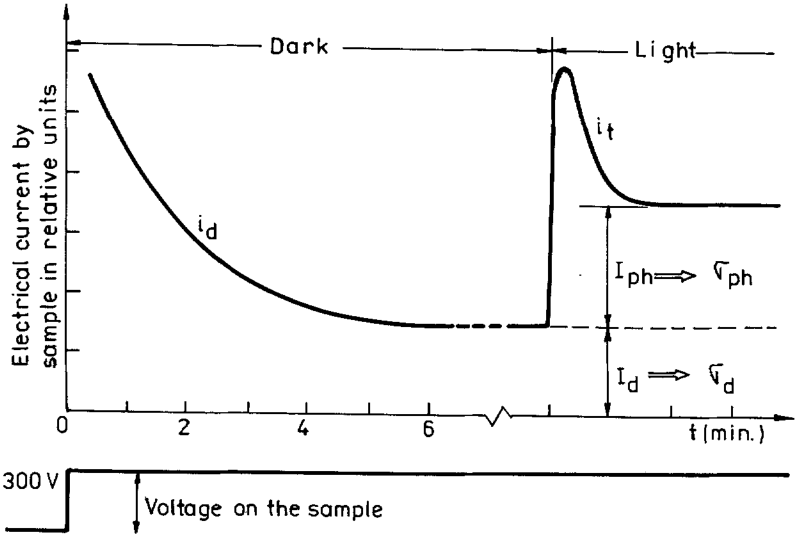


Figure 2. The time dependences of the dark current and photocurrent.

RESULTS AND DISCUSSION

The copolymer composition dependences of the dark and illumination conductions are presented in the Figure 3.

The main observation coming from the curves presented in the Figure 3 is that the photoconductivity decreases rapidly with the acceptor unit content (DNBM %) increase but shows two relative maxima,a clear one at 25-35 % DNBM and another one at 60-70 % DNBM. Taking into account the main phenomena wich determine the photoconduction and the looking of $^{*}\sigma_{ph}$ curves, the composition dependence of σ_{ph} photoconductivity could be explained by supposing that the photogeneration efficiency and the charge carrier mobility are dependent on the copolymer composition as shown in the Figure 4.

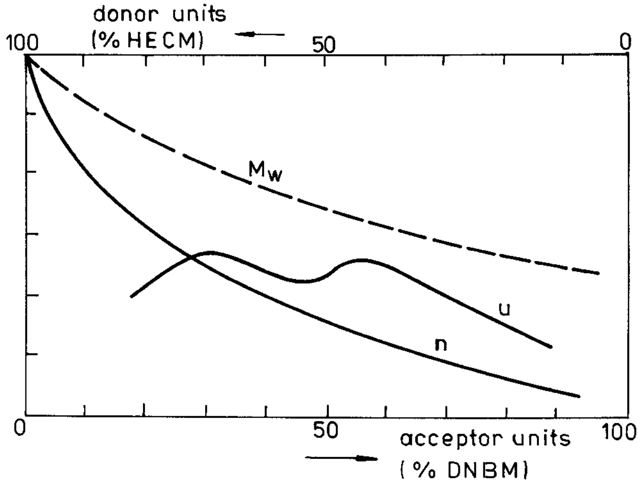


Figure 4. The copolymer composition dependences supposed for the photocarrier density into the illuminated layer (n), the mobility (μ) and the molecular weight.

The decrease of the photoinjected carrier density when the acceptor unit content increases is normal because the donor group has an ionization potential much lower than that of the acceptor group.

Another factor which could influence the electrical conduction is the length of the macromolecular chain which was found to decrease with the increase of acceptor unit content (SCHNEIDER et al. 1982).

The two relative maxima of the photoconductivity σ_{ph} could be explained if the drift carrier mobility μ has similar maxima (as shown on Figure 4). An explanation for this may result by an extention of the conclusions of studies on the charge transfer complexes of polymer - low molecular weight compound type (MORT and PAI 1976, MORT and PFISTER 1979, MORT 1980),namely:

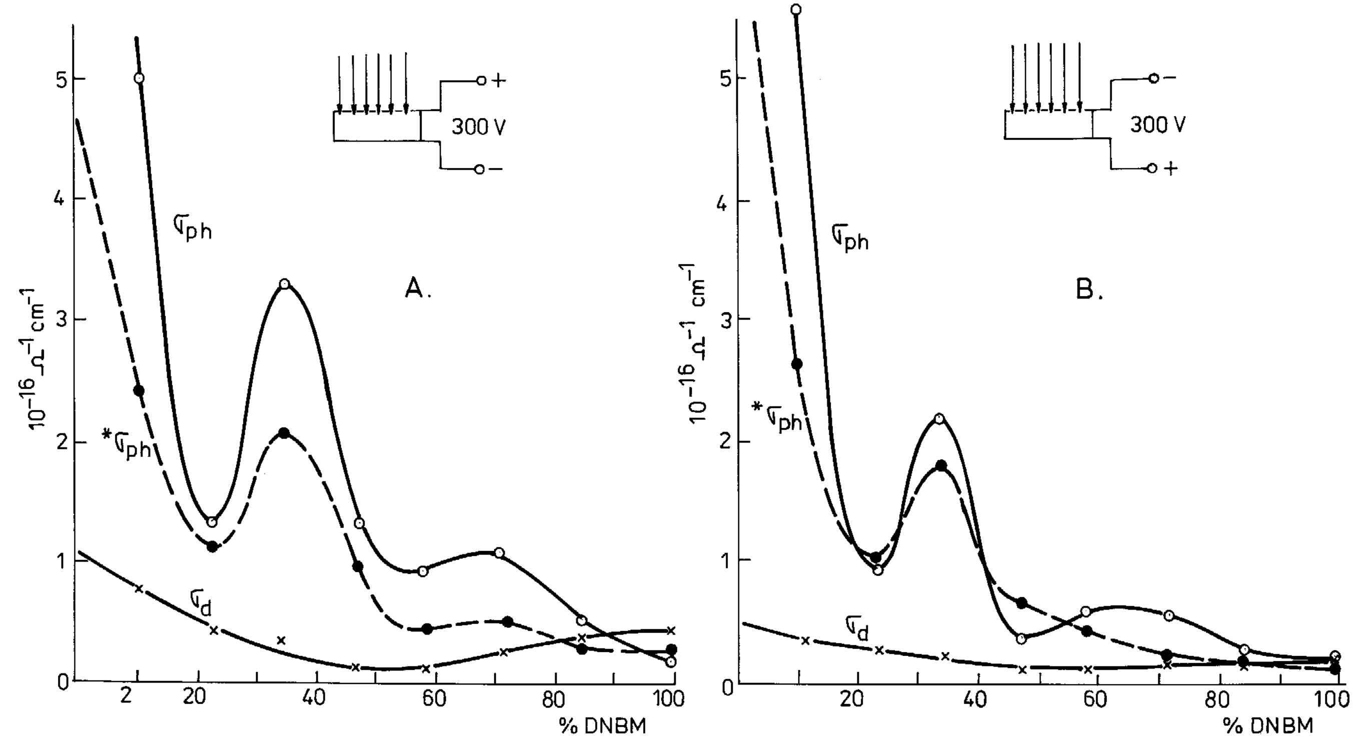
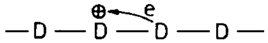
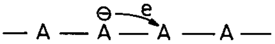


Figure 3. The dark conductivity (σ_d), the normal photoconductivity (σ_{ph}) and the photoconductivity of selenium plated samples ($*\sigma_{ph}$) against the composition of HECM - DNBM copolymers. The curves A and B are distinguished between them by the voltage polarity. Irradiation conditions: xenon lamp, 18-20 mW/cm^{-2}. Errors lower than ± 10 %. Conductivities in $10^{-16}\,\Omega^{-1}cm^{-1}$ for poly(HECM) are the followings: $\sigma_d = 1.1$; $\sigma_{ph} = 17$ and $*\sigma_{ph} = 4.6$ for the polarity A, and $\sigma_d = 0.6$: $\sigma_{ph} = 16$ and $*\sigma_{ph} = 6.0$ for the polarity B.

- the charge transport in copolymers of high donor unit content takes place mainly by holes,and the acceptor groups produce interruptions on the conduction channals,



- the charge transport in copolymers of high acceptor unit content takes place mainly by electrons,and the donor groups produce interruptions on the conduction channals,



- the acceptor and donor groups can present sensitization effects for the donor and acceptor copolymers,respectively. Such effects would be similar to the already evidenced dye sensitization effects (STOLKA and PAI,1978).

It is to be noted that an explanation based on the local order of copolymer structure is also possible because these copolymers are not totally random materials.

CONCLUSIONS

The conductivity of the HECM-DNBM copolymers determined for samples with photoinjected charge carriers by xenon lamp irradiation generally decreases when the acceptor (DNBM) unit content increses,but shows two relative maxima,a clear one at 25-35 % DNBM and a weak one at 60-70 % DNBM. The conductivity decreasing with the donor unit content can be explained by the ionization which is easier for the donor groups than for acceptor groups,and the relative maxima are due to the drift mobility of charge carriers.

The polarity of the voltage applied across the irradiated samples shows a minor effect on the photoconductivity.

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