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Section 2: Organic materials

TRANSPARENT LAYERS OF AZO–CONJUGATED POLYMERS: PREPARATION AND OPTO–ELECTRICAL PROPERTIES

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Transparent layers of poly(4,4'-azodiphenyl) and of poly(4,4'-azostilbene) with thickness of up to about 0.5 μm were obtained by vacuum thermolysis of the corresponding diazides. These films show maximum optical absorption at 400 nm where their photoconductivity is also maximum. Values of 3.2×10^{-14} S/m and 2.6×10^{-13} S/m were found for the two polymers, respectively, by irradiating films of about 0.5 μm thickness with 400 nm radiation at an irradiance of 1.7 W/m^2. An approximately linear dependence of photocurrent upon light intensity was evidenced. The photoconduction and the effect of light on the dielectric constant seem to be of real interest for applications.

Keywords: Azo-conjugated polymers, Photoconducting polymers, Photoconductive polymer films, Opto-electrical properties

1. Introduction

The polymers with alternating double bonds along the chain backbone or the so-named conjugated polymers were intensively investigated in the last twenty years because such substances show uncommon electrical conduction, as well as opto–electrical and electro-optical properties.

The principal difficulty in studying and utilization of these materials arises from the fact that they result from synthesis as insoluble and infusible powders which can be by no means processed as films or fibers. Polymer chemists try to surmount this obstacle by several methods: by using soluble (non-conjugated) precursors and inducing conjugation by a thermally activated chemical reaction, by synthesizing conjugated polymers with alkyl side chains, and by using decomposition techniques of the polymers concurrently with their synthesis [1,2].

This article presents a deposition method that allows to obtain layers of azo–conjugated polymers by the thermal decomposition of aromatic diazides in vapor state. Previously we tried to get such layers by photochemical decomposition of diazides both in solution and in vapor state. The photolysis in solution led to layers of strongly uneven surface [3] but smooth layers resulted when vapors of aromatic diazides were exposed to UV radiation in vacuum [4]. The maximum thickness of smooth layers obtained by vapor photolysis was only about 0.1 μm what created difficulties in characterization of chemical structure and morphology as well as for measurements of electrical and optical parameters.

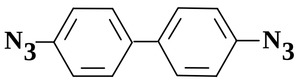
The method of azide thermolysis at low pressure which is presented further allowed us to obtain smooth layers of up to about 0.5 μm thickness with a quite good control of the process. Also, this chemical vapor deposition method may be easily integrated in the technologies currently used in microelectronics. To our knowledge there is not any reference about smooth layers of conjugated polymers with azo-linkage in the backbone.

Taking into account the fact that the azo-pigments have given good results in xerographic photoreceptor applications [2], the azo-conjugated polymers were expected to be photoconductive materials. Indeed, the layers obtained by diazide thermolysis showed pronounced opto-electrical properties.

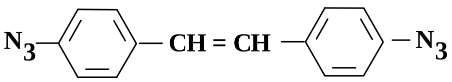
2. Experimental

2.1 Materials

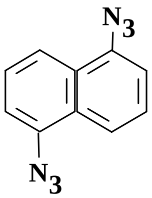
4,4′-Diazidodiphenyl (DADP), 4,4′-diazidostilbene (DASB) and 1,5-diazidonaphthalene (DANP) were used. The characteristics implied in the mentioned method were the melting point, which was 132 °C for DADP and 155 °C for DASB, and the temperature of decomposition onset, which was about 145 °C for all three azides. It is to be mentioned that DANP does not show melting before decomposition.



DADP



DASB



DANP

(1)

Devices and techniques. The polymerization of diazides to obtain thin layers of azo-polymers was carried out under vacuum (10^{-3} N/m^2) by means of the apparatus shown in Fig. 1. The evaporation furnace was composed of an electrical heater wrapped around the azide crucible (a 5 mm diameter metallic tube). A 30 mm diameter filament heater was placed between furnace and deposition support to produce an efficient decomposition of the azide molecules during their flight towards the support. With an electric power of 20 W consumed in the filament heater, it was found that a furnace–to–support distance of about 30 mm is an optimum one to get smooth layers with an acceptable deposition yield.

We found that the following procedure of heating leads to depositions of good quality: heating the evaporation furnace up to a temperature with 10 K lower than the melting point and then turning off the electric supply of the furnace and switching on the electric supply of the filament heater. Further, the temperature of the furnace slowly increases due to the radiation received from the heater. The deposition starts when the furnace temperature takes to the azide melting point at a few centigrades. Several milligrams of azide were evaporated in each experiment. Fused silica plates and Pyrex glass plates covered with transparent electrode of tin-stibium-oxide (TSO) were used for deposition of polymer layers. The area covered with polymer was of about 30 mm in diameter.

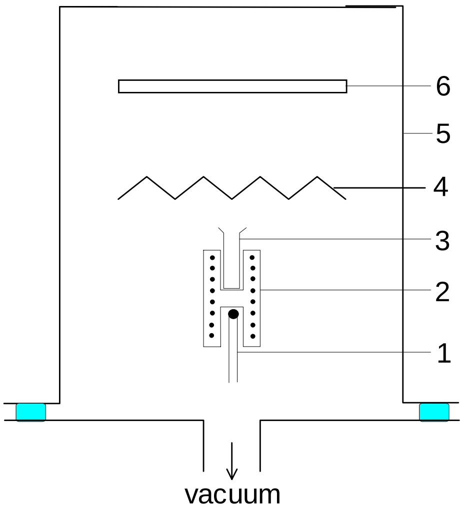


Fig. 1. Device used to obtain films by decomposition of diazides: 1 - thermocouple, 2 - electric furnace, 3 - metallic tube containing diazide, 4 - filament heater, 5 - metallic bell, 6 - condensation support.

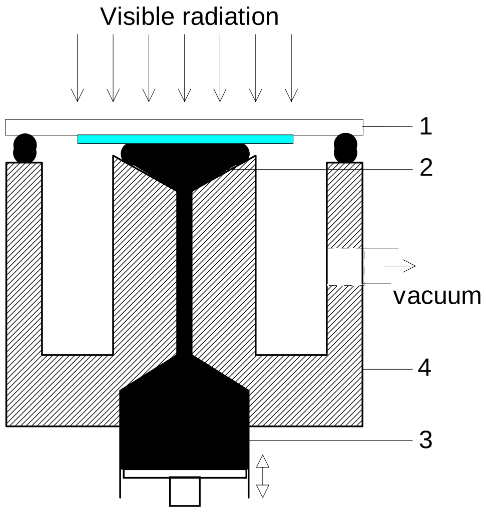


Fig. 2. Cell for photoconduction measurement: 1 - Pyrex glass plate covered with TSO electrode and azo polymer layer, 2 - mercury electrode, 3 - mercury tank, and 4 - PTFE body.

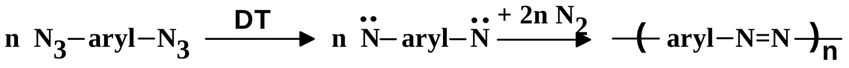
2.2 Characterization of layers

The deposited layers were amorphous, totally insoluble and thermally stable up to 400 °C. The chemical structure was established from UV-Vis absorption spectra of films grown on silica substrate. The layer surface was investigated by Atomic Force Microscopy (AFM).

Measurements of volume photoconductivity and of dielectric constant were carried out by means of the cell presented in Fig. 2. The measured samples were films deposited on TSO covered Pyrex glass plates. An illumination installation of LOS-2 type (USSR made) provided with xenon lamp of 1000 W and set of filters was used. The photocurrent and the dark current were measured by means of a Teralin III Straton electrometer.

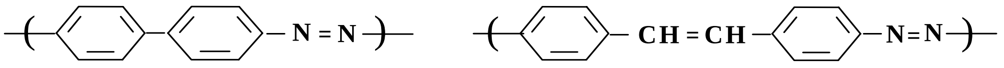
3. Results and discussion

Chemical structure of the polymer. It is well known that aromatic azides decompose in nitrene radicals. In vacuum or inert atmosphere, these highly reactive intermediaries mainly suffer recombination and reaction with azide molecules to form azoproducts [5]. On these basis, it was expected that the thermolysis of aromatic diazides performed in the mentioned conditions leads to azo-polymers according to scheme 2.



$$n\ N_3{-}\text{aryl}{-}N_3 \xrightarrow{\text{DT}} n\ \ddot{N}{-}\text{aryl}{-}\ddot{N} \xrightarrow{+\,2n\,N_2} \left(\text{aryl}{-}N{=}N \right)_n \qquad (2)$$

Indeed, the UV spectra of the films obtained from diphenyl and stilbene diazides show strong and distinct absorption bands at 400 - 430 nm (Fig. 3) which can be undoubtedly assigned to azo-aromatic chromophores. Therefore, the products resulted from these diazides are mainly azo - conjugated polymers with the structure given in scheme 3.



PADP **PASB** (3)

On the other hand, an azo - polymer structure can not be assigned to the product resulted from naphthalene diazide because its UV spectrum does not show a distinct azo absorption bond (see Fig. 3). We suppose that the failure in this case is explained by the fact that DANP decomposes before to melt

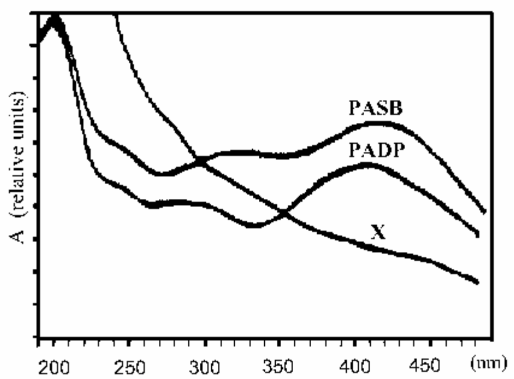


Fig. 3. UV-Vis spectra of transparent layers obtained from the three diazides. The spectrum X belongs to the layers resulted from DANP.

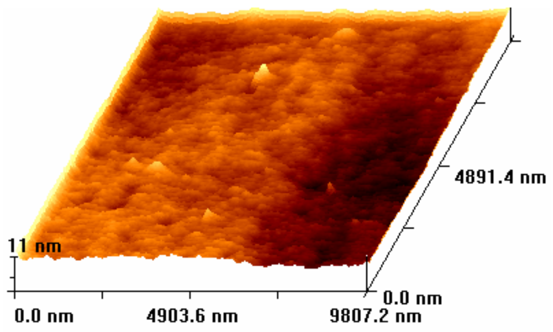


Fig. 4. AFM image from layers resulted from DADP by evaporating quantities of 3 mg.

Thickness and roughness of the films. It was observed that transparent films result if the amount of evaporated azide is smaller than about 4 mg. When larger quantities of azide were used, the deposited films showed some opacity which associates with an UV absorption at about 300 – 350 nm.

The following relationships were established for the thickness of transparent layers:

$$\text{thickness } (\mu\text{m}) \;\cong\; 0.19 \times A \;\cong\; 0.15 \times m - 0.06 \tag{4}$$

where A is the maximum absorbance of azo band and m is the mass of azide in milligrams. Absolute measurements of film thickness were carried out by AFM method.

A typical AFM image for relatively transparent films is given in Fig. 4. One observes a smooth surface with isolated and small hillocks. An explanation for the hills is that they are induced by vapor vortices [6]. The average roughness was of a few nanometers for transparent films and several tens of nanometers for "opaque" films. The opaque films show surfaces with large and irregular hills and valleys. We observed that the opacity is characteristic for films thicker than about 0.5 μm.

Photoconduction of transparent films. There will further presented measurements carried out on transparent films derived from DADP and DASB diazides, so that for samples the chemical structure of which was well established. It was observed for all measurements that the stabilization of the electric current after the light is turned ON or OFF requires several tens of seconds. Such a length of time is approximately equal with the resistance × capacitance product of the sample.

Action spectra. The dependence of photocurrent upon radiation wavelength obtained at a photon flow of 1.2×10^{18} $m^{-2}s^{-1}$ is given in Fig. 5 for the polymers PADP and PASB. As the action spectra resemble the optical absorption spectra in Fig. 3, one can be said that the photogeneration of charge carriers is mainly caused by the excitation of azo aromatic groups.

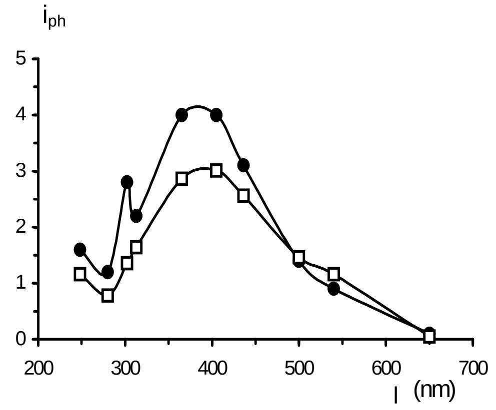


Fig. 5. Action spectra characterizing PADP (•) and PASB (□) polymers in layers of about 0.5μm thickness. Vertical scale units: pA/cm^2 for PADP and 10 pA/cm2 for PASB. Applied voltage of 1 Vd.c.

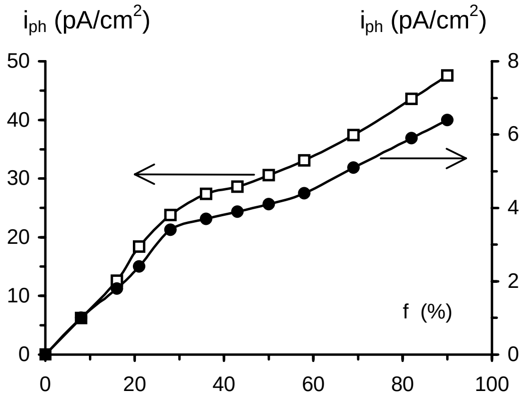


Fig. 6. Photocurrent against radiation intensity plots at 400 nm for PADP (•) and PASB (□) polymers in layers of 0.5μm thickness. f=100% corresponds to 1.7 W/m^2.

Dependence of photocurrent upon light intensity. Typical plots illustrating this dependence are given in Fig. 6. The parameter f represents the percentage of the maximum 400 nm radiation intensity which reaches the sample for a certain aperture of the apparatus slit. The curves show two approximately linear parts. As in Fig. 4, one observes that PASB films are significantly more photosensitive than PADP films, perhaps because the electronic conjugation is more efficient by C=C bonds than by N=N bonds.

Dependence of photocurrent upon electric field. A photocurrent against applied voltage plot is given in Fig. 7. This curve resembles that of a nonself–maintaining discharge in gases, what suggests an useful model to describe the photoconduction process in polymers.

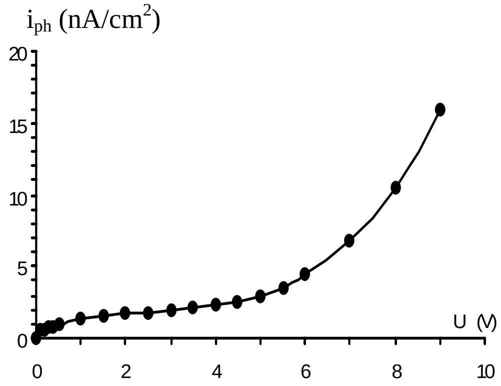


Fig. 7. Photocurrent - voltage plot over a wide range of electric fields for a PADP layer with thickness of about 0.5 μm and exposed to a 50 W incandescent lamp at 12 cm distance.

Dielectric constant. We observed a significant diminution of the dielectric constant when azo polymer films are illuminated. For example, a PADP layer of about 0.5 μm thickness showed $\varepsilon = 1.9$ in dark and $\varepsilon = 1.6$ when it was exposed at a 25 W incandescent lamp placed at about 10 cm. Such a property seems to be more attractive for applications than the photoresistive effect.

4. Conclusions

Smooth layers of poly(4,4'-azodiphenyl) and of poly(4,4'-azostilbene) can be obtained by thermal decomposition in vacuum of the corresponding diazides. The film smoothness and chemical purity were rather high when the evaporation rate was low and the films were thinner than about 0.5 μm. These polymers are real photoconductors between 350 and 600 nm. The photoconductivity is nearly proportional to the light intensity and depends on the polymer structure. The dark conductivity was about 5×10^{-17} S/cm. Depending on the light intensity and wavelength, the ratio of photocurrent to dark current was found with values from units to thousands. Important modifications of the dielectric constant under illumination were also observed.

Acknowledgement

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References

[1] J. L. Bredas, R. R. Chance, Eds, Conjugated Polymeric Materials: Opportunities in Electronics, Opto-electronics and Molecular Electronics, Kluwer Academic, Dordrecht, 1990.
[2] H. S. Nalwa, Ed, Handbook of Organic Conductive Molecules and Polymers, Wiley, New York, 1997.
[3] V. Barboiu, D. Timpu, E. Rusu, A. Airinei, Polym. Adv. Technol., **9**, p.629-634, (1998).
[4] V. Barboiu, D. Timpu, E. Rusu, A. Airinei, Macromolec. Symp., in press.
[5] S. Patai, Ed., The Chemistry of Azido Groups, Wiley Interscience, New York, 1971.
[6] E. W. Meijer, S. Nijhuis, F. C. B. M. van Vronhoven, E.E.Harings, in reference 1, p115.