Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 17 Oct 2011.

To cite this article: Piergiulio Di Marco , Gabriele Giro , Silvano Lora & Mario Gleria (1985): Photoconductive Properties of Some Polyorganophosphazenes Doped With Trinitrofluorenone, Molecular Crystals and Liquid Crystals, 118:1, 439-442

To link to this article: http://dx.doi.org/10.1080/00268948508076254

Mol. Cryst. Liq. Cryst. 1985, Vol. 118, pp. 439-442
0026-8941/85/1184-0439/$10.00/0

Printed in the United States of America

PHOTOCONDUCTIVE PROPERTIES OF SOME POLYORGANOPHOSPHAZENES DOPED WITH TRINITROFLUORENONE

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Abstract Polyorganophosphazenes are electrical insulators and in general non photoconducting polymers. The doping with trinitrofluorenone changes their optical and electrical characteristics: new optical absorption bands appear in the visible region and the doped polymers show photoconductive properties. The photoresponse seems to be related to the nature of the organic group attached to the polymer chain.

INTRODUCTION

Polydichlorophosphazene consists of an alternating sequence of P and N atoms, with two Cl atoms attached to each phosphorous (fig.1). X-ray diffraction techniques provided evidence of a cis-trans planar type of structure, with a polymer repeating distance along the fiber axis of 4.92 A [1].

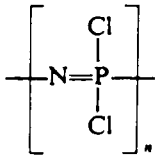


FIGURE 1 Structural formula of polydichlorophosphazene

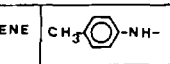
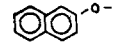
In polyorganophosphazenes the Cl atoms are substituted with suitable organic groups and in principle, by a careful choice of the substituents, any set of required physical property can be designed. In general these polymers possess a high molecular weight, high thermal resistence, high stability to

uv and visible radiation. Their doping with trinitrofluorenone (TNF) proves to be, in some cases, a useful method for obtaining materials with good photoconductive properties in the uv and visible range.

EXPERIMENTAL

The polyorganophosphazenes used in these experiments and reported in Table I were doped with a high concentration of TNF (0.4 to 2 TNF molecules for 1 polymer monomeric unit). The complex was prepared by dissolving the polymer and the TNF in a mixture of toluene and cyclohexanone. A sandwich cell arrangement was used for the electrical measurements. The complex solution was coated on a semitransparent layer of Al deposited on a quartz plate; the film obtained (2-10 μm thick) was heat cured for the removal of the solvent. A second metal layer completed the sandwich.

TABLE I Polymers used and formula of the organic substituent

POLY[BIS (P-TOLYLAMINO)] PHOSPHAZENE		PBT
POLY[BIS (2-NAPHTHOXY)] PHOSPHAZENE		PBN

The electrical measurements were performed using a Keithley 610B electrometer and a Fluke 412B power supply. The sandwich cell was placed inside a screened container having a quartz window for the entrance of the light coming from a Xenon 900 W and filtered with a Hilgher & Watts monochromator. The light intensity was measured with an EG & G 460 laser power meter.

OPTICAL AND ELECTRICAL PROPERTIES

Undoped polymers: the substituent is responsible for the absorption at wavelenghts higher than 200 nm. The polymers are electrical insulators, with a resistivity comprised between 10^{14} and 10^{16} ohm.cm and don't show any appreciable photoconductivity.

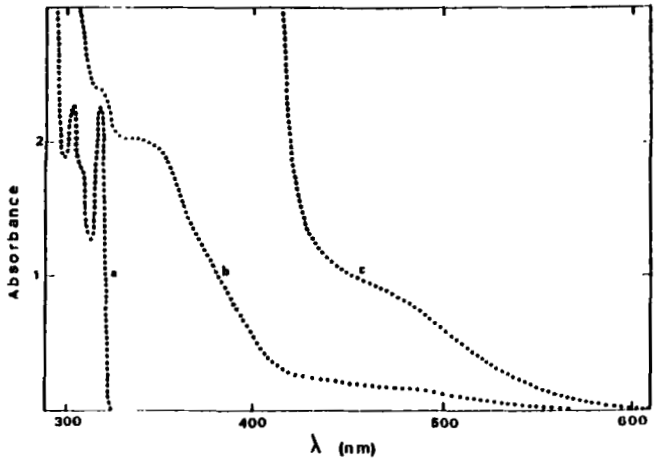


FIGURE 2 Absorption spectra of: a PBN film, b PBN-TNF film, c C.T. complex between 2-naphthol and TNF in toluene.

Doped polymers: figure 2 shows the appearence of a new absorption band in the visible region, due to C.T. formation between substituent groups and TNF.

The dark conductivity increases of 2÷4 order of magnitude. When irradiated with visible or uv light, the doped material shows an increase of the electrical conductivity; the best results are obtained with PBN-TNF 1:1, where a photocurrent density of 10^{-6} A/cm^2 is reached, with 5×10^{13} photons/cm^2 impinging on the cell, at 450 nm, with an applied field of 10^5 V/cm.

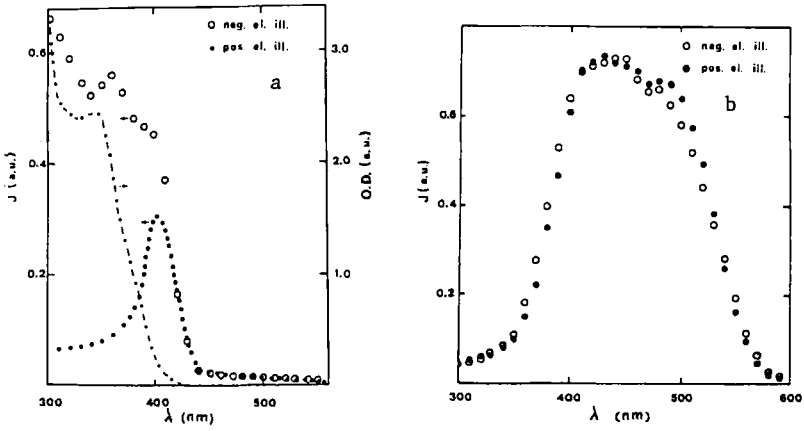


FIGURE 3 Photocurrent action spectra of : a PBT-TNF 1:1, b PBN-TNF 1:1.

The action spectrum of PBT-TNF indicates clearly that the exciton-surface mechanism of charge generation is involved and that the electrons are the majority carriers, whereas the action spectrum of PBN-TNF shows a strong sensitization effect in the spectral region where the light is absorbed only by the C.T. (the long wavelenght cutoff of TNF absorption is at 450 nm).

Two possible explanations exist for this effect: (a) photodetrapping of trapped carriers or (b) photogeneration of charge pairs through the excited C.T. complex.

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1. E. Giglio, F. Pompa and A. Ripamonti, J. Polym. Sci., 59, 293, (1962).

This work was carried out under the research program " Progetto finalizzato Chimica Fine e Secondaria " of CNR.