

Homo polymerization and co-polymerization of n-pentenyl carbazole (N-PCz) by cold plasma and radicalic polymerization (glow discharges)

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ABSTRACT

In the present study, we present two homo-polymers, synthesized from 9.N-vinyl carbazole derivative with a vinylic side chain; $[-(\text{CH}_2)_m-(\text{CH}=\text{CH}_2)-]$; where $m = 3$ and some copolymers. Plasma Enhanced Vapour Deposition (PECVD) was used to obtain homopolymer thin films. The molecular orbital calculus (MO), and the chart, showing the synthesis of these compounds, were reported elsewhere¹.

Key words: Electrophotographie, charge transfer, donor of electrons: acceptor of electrons, donor-acceptor complexes, cold plasma, thin film deposition.

INTRODUCTION

The polymers organic photoconductors are widely employed in electronic devices, like inorganic ones. These compounds have the advantage on mineral compounds because they are more malleable; can be obtained in crystal forms, chippers and with growing photoconductor yields.

The gaining of their importance is traduced by the huge number of works published nowadays and the multiplicity of their use in different technologies.

Photoconduction in Polymers

Basic principles of photoconductivity

The process of photoconductivity involves several steps:

Radiations and formation of excitons, adsorption

The photoconductor effect may be induced in majority of polymers containing aromatic cycles, if they are submitted to radiations having energies near their absorption spectrum. This radiation had to contain sufficient energy for promoting electronic transitions in the polymer; which is the base of the

phenomenon of the photoconduction². Consequently, the radiation of light energy, (X rays- γ rays and neutron rays), can induce photoconductivity in the same manner as a flux of light hits on an appropriate polymer film or sheet. Knowing that the energy of photons decreases, from UV; VIZ and IR. Many polymers cannot manifest the phenomenon of photoconductivity; because of the incident energy is not sufficiently enough to excite the electronic transition. Thus, in order to produce charge carriers by visible light sensitising dyes or electron acceptors forming coloured charge transfer complexes have to be added³.

The polymers that can transit their electrons in the domains of UV-VIZ or the IR are in general insoluble or infusible things that rend them difficult to manipulate. To enlarge the adsorption spectrum of soluble polymers, which manifests a photo response when they are submitted to radiations of VIZ spectrum, the modification of the polymer state had been is indispensable. This modification was obtained by adding some adjuvant, said sensibilizers⁴ which are classified as follows:

Optic sensibilizers

This system is obtained by the addition of some dyes to the polymer, to introduce some regions of light adsorption that adds to the existent regions.

Inorganic sensibilizers

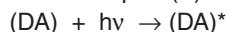
The most inorganic compounds were used as sensibilizers when they are coated as thin films on the polymers as, selenium (Se), Zinc oxide (ZnO_2), zinc sulphate crystals ($ZnSO_4$), and alloy of Siliceous, Titanium, Astatine (SE-Te-As).

Sensibilisation by charge transfer complexes, (CTC)

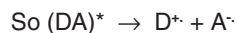
The charge transfer complexes are constituted from polymers, as donors of electrons (D) doped by a substance having properties of accepting electrons, sad acceptors (A).

From the complexes Donors Acceptors, results an electron transfer from the upper orbital of the donor, to the lower orbital of the acceptor. For example, the aromatic polymers like poly-naphthalene, polystyrene and polyvinyl carbazole, makes complexes with tri-nitro-fluorenone and give CTC.

To explain the photo generation mechanisms of the holder of charges; Cr. Semionescu and col.⁶, proposed as coming, electron donor (D) + electron acceptor (A) \rightarrow (DA)



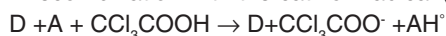
(DA)* is the excited CTC complex, $h\nu$ is the energy adsorbed by the CTC complexe.



$D^{\cdot+}$ and $A^{\cdot-}$ Are radical ions (holder of charges).

This mechanism is based on the subsequent facts⁶

1. The augmentation of the ESR signals by illumination of the CTC. The origin of ESR signal is the ion-radical $D^{\cdot+}$ and $A^{\cdot-}$
2. Williams⁷ had found that the addition of the tri-chloride acetic acid to the CTC gives a proton to the ion- radical, which prevent the recombination with the cation-radical ($D^{\cdot+}$)



Generation of charge carriers

By the adsorption of light the active groups are excited and from closely bound electron-hole pairs, i.e. excitons. The excitons are captured and dissociated at the donor/acceptor sites as a result of functional groups that are polarized and appropriately to cause charge separation. The key process that determines the overall photogeneration efficiency is electric field induced separation of excitons into the free charge carriers. Both intrinsic and extrinsic photogeneration of charge carriers in polymers under illumination is discussed in detail in the review⁸.

Injection of carrier

An injection of carriers occurs only if an extrinsic photo generator is used together with a charge transporting material. Usually dye particles are dispersed in a polymer matrix or evaporated on top on conductive substrate and then covered with the charge-transporting polymer. The carriers are generated in the visible light-adsorbing material and injected into the polymer. Charge injection, as photogeneration and charge transport, is electric-field-dependent.

Carrier transport

The photogenerated or injected charge carriers move within the polymer under the influence of electric field. In this process the photoconductive species, for example carbazole groups in the polymer, pass electrons to the electrode in the first step and thereby become cation radicals. Cation radicals of PCz are stabilised by the charge (hole) resonance between more than two neighbouring chromophores^{9,10}.

The transport carriers can now be regarded as a thermally activated hopping process, in which the whole hops from one localised site to another, in the hole of the electric field (Fig. 1).

The moving cation radical, can accept an electron, from the neighbouring neutral carbazole group, which in turn becomes a hole. Effectively the hole moves within the material, while electrons only jump among neighbouring species. In a more chemical terminology, hole transport can therefore be described as a series of redox reactions among equivalent groups.

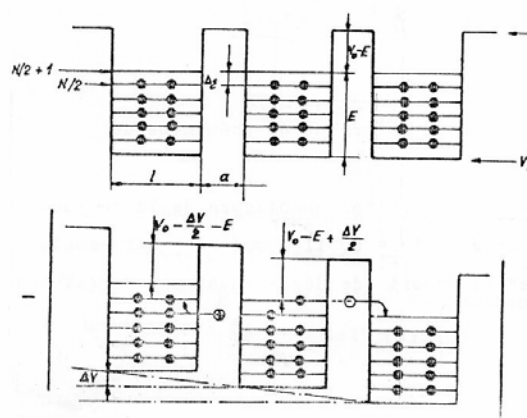


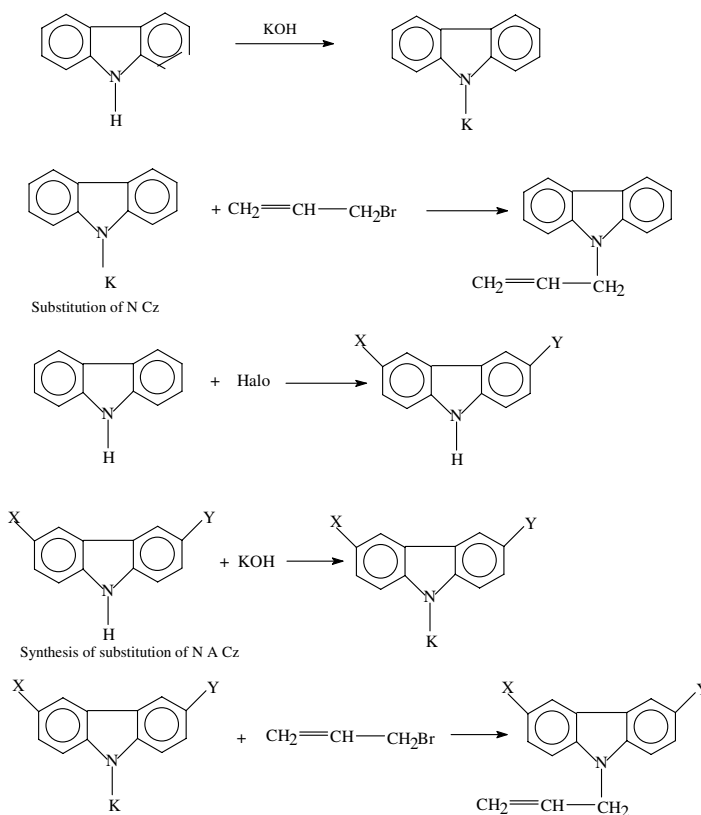
Fig. 1: Representing the Holes of the electric field

Recombination

Coulomb forces eventually cause recombination of free electrons and holes at recombination sites in the circuit. The process competes with the generation of charge carriers.

Trapping

During transit, the carriers do not move with the uniform velocity but resides most of the time in localised states (traps) and only occasionally are released from these traps to move in field direction. The traps can be shallow or deep. These terms are only relative, and refer to the release times. Shallow traps are those from which carriers are released in the time of experiment. The trapping process is responsible for the extremely charge carrier mobility in most of the polymers. The mobility is usually, electric field and temperature dependent. For PVK the room temperature mobility is ranging from 10^{-8} to 10^{-6} cm^2/Vs at an electric field (E) of 105 V/cm have been reported¹¹.



Scheme 1: represents carbazole derivatives

For the characterisation of charge-transport properties, two established methods exist:

1. The time of flight (TOF) technique, based on transient photocurrent measurements,
2. And the xerographic method, based on photo induced discharge measurements¹².

With this in mind, we started the preparation of a series of carbazole-containing polymers and some low-molecular-weight model compounds which shall be used in the investigation of the structure property relationship. For that purpose, polymers in which certain parameters can be varied systematically are required. Scheme I shows a schematic representation of such a system. In those polymers, the making chain, the spacer that decouples the motion of the photoconductive group and the backbone, and the photoconductive group itself can be varied. Scheme I. Recently we have described the preparation of series of poly vinyl derivatives with pendent carbazolyl groups scheme II,¹³.

In these polymers the carbazolyl moiety is separated from the backbone by spacer containing of 1, 2 and 3 methylene groups.

The spacer length has an influence on some physical properties of the polymer as e.g. the glass transition temperature witch drops from I a, to I c.

This paper describes the photoconductive properties of the polyvinyl I a-c which were investigated by the time-of-flight method.

EXPERIMENTAL

Homo- polymerisation of N-pentenylcarbazole (NPCz), by cold plasma, (Glow discharge)

Plasma Enhanced Chemical Vapour Deposition (PECVD) is a widely used plasma process, to deposit various thin films on almost any kind of substrates (semi-conductor, silica, glass, polymers, steel...). Since PECVD allows deposition at low substrate temperatures and leads to films with unique properties which can not be obtained by conventional deposition techniques, it finds applications in many fields such as microelectronics, automobile, aeronautic, food packaging or

biomaterial industries.

1- two necked balloon in pyrex glass, 2- brass curved electrodes, 3- source of radio frequencies, 4- to vacuum pump, 5- solvent trapping, 6- to manometer and air inlet.

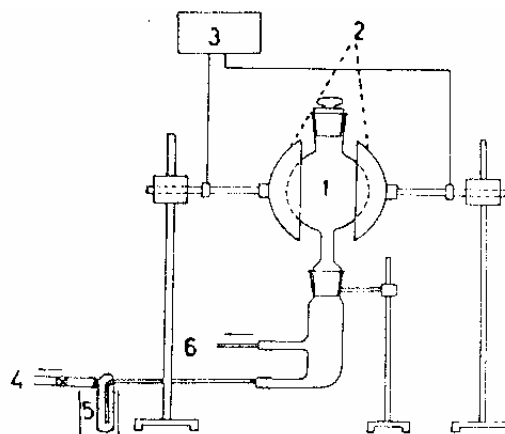


Fig. 2: Represent the device of glow discharge

Procedure

A quantity of solid monomer (0.3g) was put in the rounded flask and a small quantity (5 to 10ml) of di-ethylether, sufficiently to dissolve the solid monomer are introduced in balloon 1. The balloon was inclined and slowly rotated, till the evaporation of all the solvent, so we obtained a thin film deposited on the internal surface. The balloon was integrated in the system and the evacuated till constant vacuum (2 to 0.5 tore) under the radio frequencies (10 to 11 MHz), till the apparition of a green-blue glow (beginning of the reaction) in a period time of 5 to 60 sec. The reaction is ended when the glow takes pale color.

Homo and co- polymerisation of N-pentenylcarbazole (NPCz), by radical initiation: Material purifications and synthesis.

Monomers

- The NPCz monomer was re-crystallized in anhydride methanol dried under high vacuum at 40°C.
- The MA monomer was re-crystallized from CHCl₃ anhydride and dried under vacuum at room temperature.
- The phenyl-maleine-imide was synthesised¹⁴.

The Azo-Iso-Butyro-Nitryl (AIBN), was re-crystallized from dried methanol and dried under vacuum for 48 Hs.

The solvent, (toluene), was refluxed on

metallic sodium during three days and distilled on CaH_2 before use.

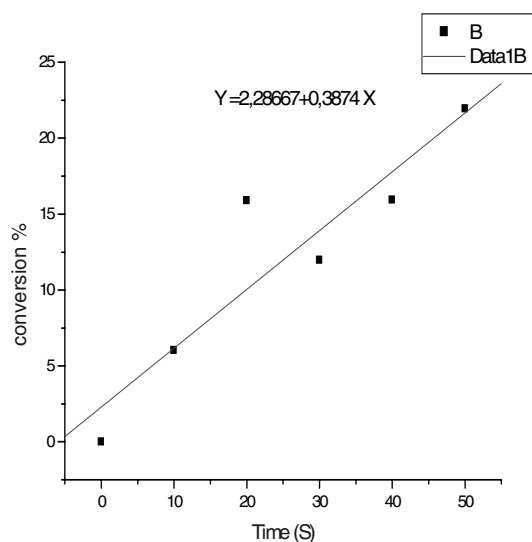
The dioxane solvent was dried for a week and distilled on KOH.

Table 1: % polymerisation yield/time of polymerisation

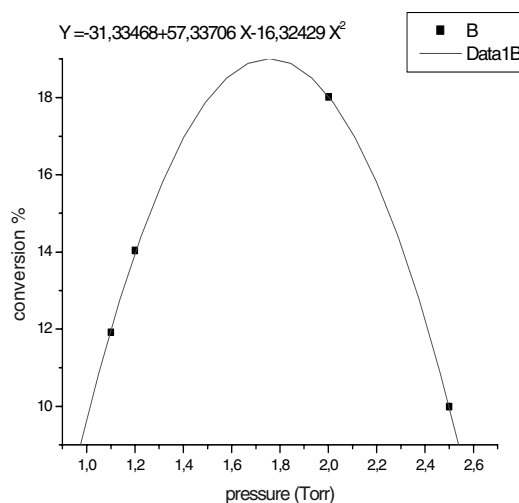
Yield %	Time in sec.	Experiment N°
6,04	10	1
15,90	20	2
11,99	30	3
15,94	40	4
21,96	50	5
25,86	60	6

Table 2: % Yield/ Pressure

Yield %	Pressure in tore	Experiment N°
9,99	2,5	1
18,02	2,0	2
14,04	1,2	3
11,92	1,1	4
12,01	1,0	5



Graph 1: % Polymerisation diagram



Graph 2: % Conversion/Pressures diagram

Polymerisation in mass

In a reaction glass vial, Fig. 3; 4.7 gr. ($2 \cdot 10^{-2}$ mole) of the monomer and 0,2 gr. of AIBN as initiator were introduced. The mixture was heated at a constant temperature of 115°C for 6 hours. We obtained a solid brown masse. This masse was dissolved in 5 ml of toluene and poured after that in methanol as precipitant. The polymer of white colour was obtained with 5 % of yield and a fusion point (f.p) of $101-110^\circ\text{C}$.

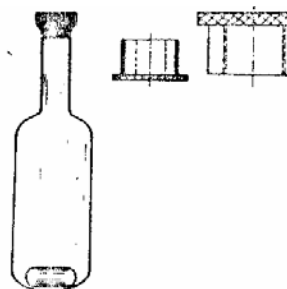


Fig. 3: Reaction glass vial

Table 3: Elementary Analysis of poly-NPCz obtained by cold Plasma, (Glow discharge)

N	H	C	%
7.26	5.69	88.04	calculated
7.54	6.26	86.18	found

The IR characteristic adsorption bands of vinyl groups are: in the plane ($1410-1420-1290-1300\text{ cm}^{-1}$) and out of plane ($990-910\text{ cm}^{-1}$), the existence also of the deformation vibrations of $-\text{CH}_2$ and $-\text{CH}$ group, (1460 cm^{-1}). This adsorption proves that the polymer was obtained.

Polymerisation in solution

In a three necked rounded bottom flask of 100 ml, a solution of 4.7 gr. (2.10^{-2} mole.) on NPC and 0.047 gr. of AIBN as catalysis in 47 ml toluene anhydride. The solution was stirred for 24 hours at constant 98°C . After concentration by evaporation, the solution was pored in methanol; the yield was of 3%.

Solution polymerisation initiated by *di-tertio-butyl-peroxide* (DTBP)

2 gr. of NPC and 0.2 ml of DTBP in 20 ml *n*-octane were introduced in the reaction vial, fig. The time and the reaction temperature were of 24 Hs and 130°C respectively. The polymer was precipitated in methanol and the yield was of 52%.

Reaction of co-polymerisation.

Reactions of co-polymerisation were made to determine the reactivity of the N-pentenyl carbazole monomer and to obtain alternated copolymers by the use of the phenylmaleimide (PhMI) and maleic anhydride (MA) as co-monomers. III-1-3. Polymerisation procedure

The copolymerisation reaction was effectuated under closed system, as previously cited. The co-monomer report was mol/mol, 10:1, solvent monomer and monomer initiator, 100:1.

1,175 gr. ($10.5 \cdot 10^{-3}$ mol) NPCz, 0.865 gr. ($0.5 \cdot 10^{-3}$ mol) (Ph MI) and 0.408 gr. AIBN were introduced in the reaction vial. The glass vial, hermetically closed, was put in an oil bath and

magnetically agitated during 12 Hs and the temperature of reaction was maintained constant at 110°C . The reaction solution was slowly pored in methanol, filtered and washed with hot methanol. A white copolymer was obtained, after drying under vacuum at 40°C , with a yield of 32 %, a point of fusion (f.p) of $144-152^\circ\text{C}$ with an intrinsic viscosity $[\eta] = 0,039\text{ dl/gr}$.

The characteristic IR adsorption bands are: $2860-2925\text{ cm}^{-1}$ (d CH aliph.), $1700-1770\text{ cm}^{-1}$ (d CO imide), 3050 cm^{-1} (d CH arom.), absence of vinyl groups ($1410-1420, 1290-1300, 910-990\text{ cm}^{-1}$).

The NMR signals: 1,6 – 2 ppm for ($-\text{CH}_2-\text{CN}$), 3,2 – 3,5 ppm for (CH-CO), 4,1 – 4,3 ppm concerns (CH_2-N) and 6,5 – 7,8 ppm to (CH arom.).

Copolymerisation of N- pentenylcarbazole (NPCz) with maleique anhydride (AM)

Having electron attractor substituents, maleimide and maleic anhydride are monomers highly acceptor of electrons and can give alternating co-polymers with pentenyl carbasole (NPCz).

In this reaction of copolymerisation 2.3 gr. (10^{-2} mol) NPCz, 0.98 gr. (10^{-2} mol) AM were used in 20 ml dioxane as solvent containing 0.17 gr. di-tertio-butyl- peroxide (DTBP) as catalysis, at a constant temperature of 120°C , during 12 Hs. The yield of reaction was 38%, the point of fusion of the copolymer = $160-163^\circ\text{C}$ and $[\eta] = 0.028\text{ dl/gr}$.

Characteristic bands of IR: 3050 cm^{-1} (CH arom.), $2940 - 2885\text{ cm}^{-1}$ (CH al.), $1865-1785\text{ cm}^{-1}$ (δ CO sym. and anti-sym.), 1600 cm^{-1} (δ C = C), 1460 cm^{-1} (δ CH_2), 1330 cm^{-1} (δ -CH).

NMR signals: 0,8- 2,9 ppm (CH- CH_2 -), 3,3 -4,5 ppm (CH-CO), 5,28 ppm (CH_2-N), 6,5-8 (CH arom.). In table 4, we represent the different compounds of polymerisation and copolymerisation of NPCz, some physical characteristics and the results of elementary analysis.

The form 1 to 3, were white substances, with a low degree of polymerisation and the IR and NMR spectrums confirm the structures of PNPC an the copolymers of the last named.

Table 4: Represents the of polymerisation and copolymerisation of NPCz, intrinsec viscosity and the results of elementary analysis

Product	°C- intervals	Intrin Viscosity	Elementary Analysis % N
1: poly NPCz	101-105	M = 1400	5, 97
2: copolym. (NPCz+PhMI)	144-159	0,039	6,86
3: copolym. (NPCz-AM)	160-163	0,028	7,48

RESULTS AND DISCUSSION

The synthesis of these monomers were made by the condensation of alkyl carbazole of (Na or K), and pentenyl bromide. The copolymerisation was successfully obtained and analysed.

The synthesis of some monomers, homologous of vinyl carbazole, with a side aliphatic chain of five carbons, mono-substituted and di-substituted in the carbazolic nucleus gave a spaced polymers.

The IR and NMR spectrums evidenced some spectral characteristics which confirm the chemical structures attributed to the synthesised monomers.

The thermo-differential analysis done (TDA) conducted to some important conclusions on the stabilities pentenylic derived monomer under the effect of temperature. By varying the pressure we obtained soluble polymers with enhanced yields. And the elementary analysis confirmed the absence of oxygen.

Annexe : Representing the IR, NMR and TDA; TDG Spectrums of the synthesized polymers

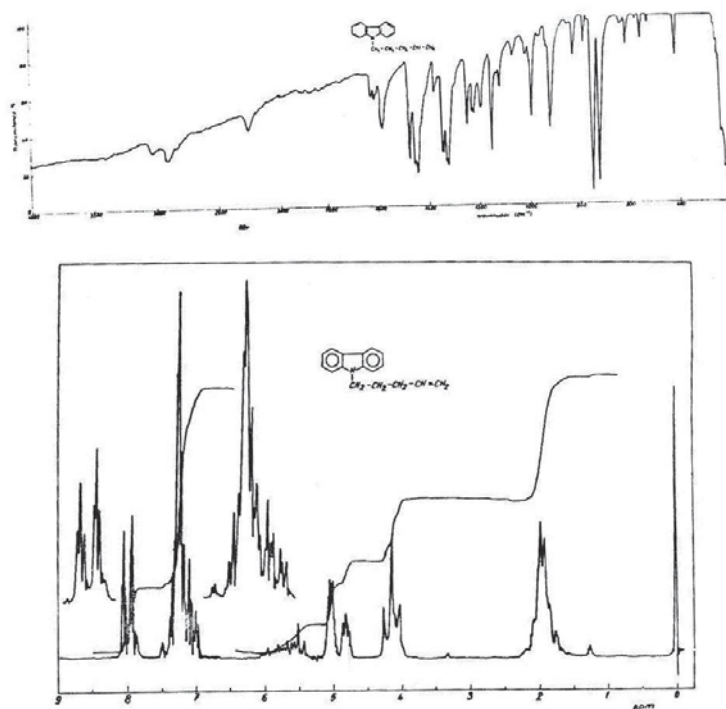


Fig. 1 : Spectrums of IR & NMR for Pentenyl Carbazole

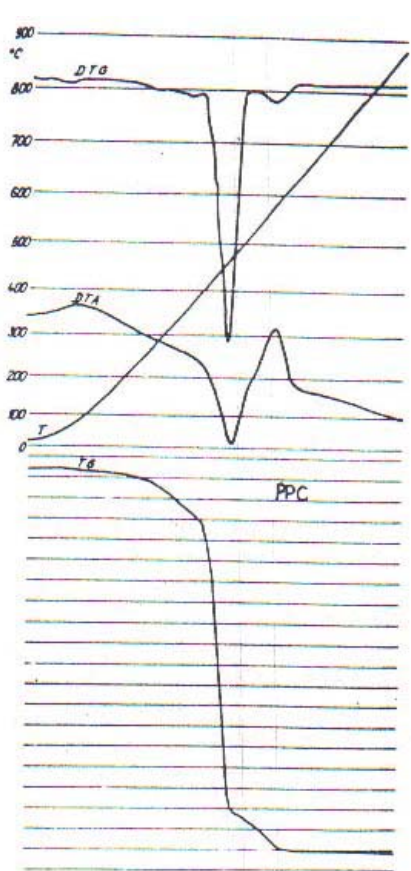


Fig. 2: ATG & ADT Spectrum of poly-pentenyl carbazole

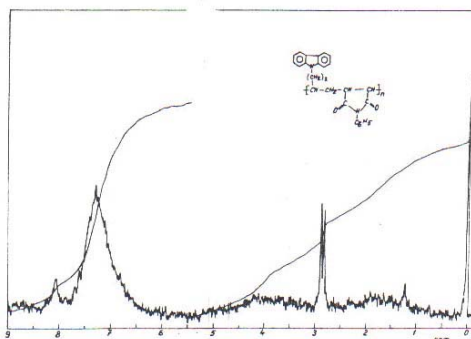
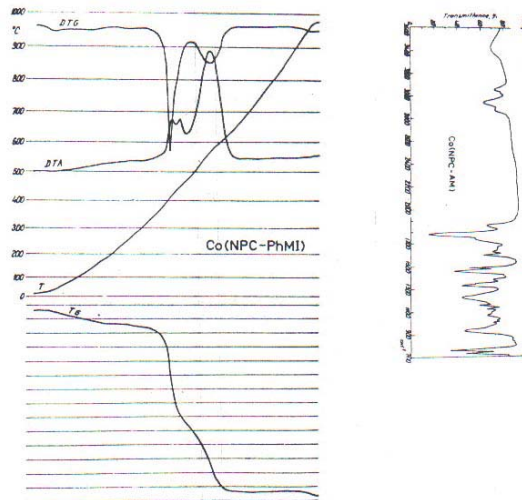


Fig. 3: Spectrums: IR, NMR, DTG and ADT of the p-N.PCz polymer oc-phenyl imidazole

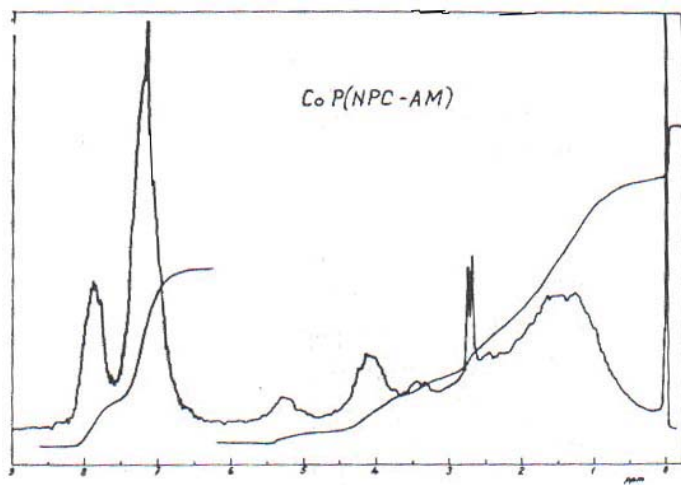


Fig. 4: NMR spectrum of Copolymer- pentenyl carbazole/acryl amide

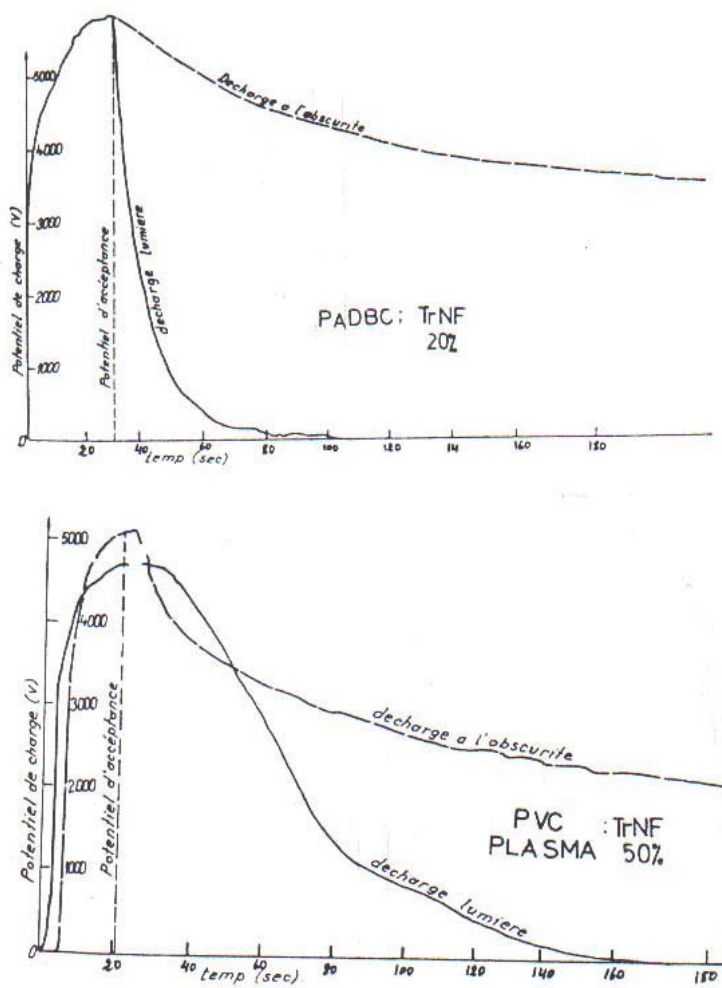


Fig. 5: Graph of the electronic discharges in light and in the dark. For the poly-penteylcarbazol (Donor) with trinitroflorenone (Acceptor)

CONCLUSIONS

- Elaboration of a system of polymerization for solid monomers, initiated by radio frequencies.
- By this method we obtained soluble polymers of pNVCz and pNPCz.
- The structure of obtained polymers were established by elementary and

spectrographic analysis; also the average molecular mass, the thermal stabilities and activation energies were determined.

The possibilities of application of the obtained polymers a copolymers in xerographic and photovoltaic systems were studied and the curves of surface potential discharges, in dark and light (technique of flight) were traced.

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