

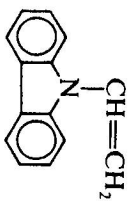
PLASMA POLYMERIZED POLY(N-VINYLCARBAZOLE) THIN FILMS¹⁾

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Thin films were prepared by polymerization of N-vinylcarbazole vapours in an a.c. glow discharge. Basic structural characteristics obtained from Transmission data in the ultraviolet, visible and infrared regions and from ESCA analysis are compared with the features of a conventional solution-grown polymer. Possible applications in recent electrography are discussed.

1. INTRODUCTION

Among the organic photoconducing systems the poly(N-vinylcarbazole) (PVK) has attracted special attention. In the case of conventional solution-grown polymers the influence of structure and morphology on the electronic properties has been intensively studied [1—3]. In several recent works the photogeneration process in a conventional PVK and in a plasma polymerized N-vinylcarbazole (PPVK) has been compared [3, 4]. The present paper concentrates on the structural characteristics and optical properties of the polymer films obtained by plasma polymerization of N-vinylcarbazole



monomer vapours in an a.c. glow discharge.

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II. EXPERIMENTAL DETAILS

II.1. Film Deposition

The films were deposited in a system consisting of two vertical parallel aluminium electrodes (60 mm in diameter, 22 mm distance) placed in a glass cylinder vessel (120 mm in diameter, 200 mm high). Prior to deposition, the reaction space was evacuated by a diffusion pump to a base pressure, the $\sim 10^{-3}$ Pa. After closing the pumping valve argon was admitted to a pressure of 27 Pa and a discharge was excited by an a.c. signal supplied from an RC generator (BM 344, Tesla) and a home made amplifier. The monomer vapours were introduced into the plasma region from a resistively heated stainless steel evaporation source 30 mm below the electrodes. The evaporator temperature (usually within 60°C and 250°C) was controlled by an iron-constantan thermocouple. The substrates were mounted on the electrodes.

For comparison, samples were also prepared from a solution formed by a PVK (Luvican) dissolved in a toluene: cyclohexanone (4:1) mixture.

II.2. Film analysis

The optical transmission of the films deposited on fused quartz substrates was measured in a double beam CF4 (Optica Milano) spectrophotometer. The spectra of the films on polished KBr single crystals were recorded in a Fourier transform IFS-85 (Bruker) spectrometer. The surface of the films deposited on an aluminium foil was examined by ESCA in an ESCA-3 (VG-Scientific) spectrometer using Al-K_α X-ray irradiation. The film thickness was determined by a Tencor profilometer.

III. RESULTS AND DISCUSSION

The parameters of polymer films used for the analysis presented in this work are summarized in Table I. In the first series of experiments the films were plasma polymerized at various power values (voltage between the electrodes times the discharge current), frequencies and deposition durations (samples A—D). For comparison, solution grown films were prepared (samples E, F) and studied after their introduction into a discharge in argon (sample F).

The transmission of films in the near uv. and visible regions is shown in Fig. 1. Higher absorption in the visible region for plasma polymers documents the typical crosslinked structure. All the samples exhibit the main absorption edge near 350 nm. A slight shift of the absorption edge (about 8 nm) to lower wavelengths for PPVK samples gives evidence of a lower concentration of possible absorption centres.

Summary of the deposition conditions of PPVK and PVK films and their thicknesses.

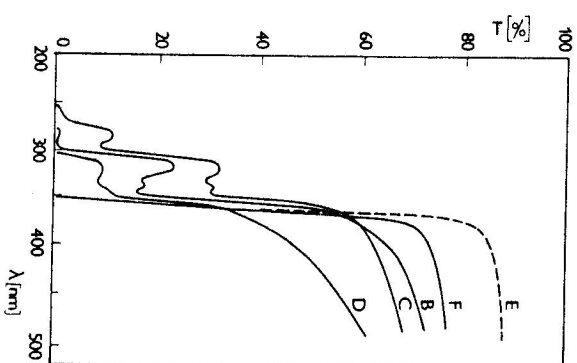
Table I

Sample No	Specification	Frequency kHz	Power W	Deposition duration min	Thickness μm
A	plasma polymerization	40	12.9	6	0.2
B		5	1.3	6	0.4
C		40	8.8	7	0.5
D		40	8.5	8.5	0.6
E	solution grown				
F*		40	9.9	20	5.0
					5.0

* Ar discharge

Local absorption maxima at 346 nm, 332 nm, 300 nm and 250 nm may be observed in the uv. region in the case of PPVK samples which are substantially thinner than their solution-grown counterparts. In conventional PVK the absorption on carbazole groups in the regions within 350—300 nm, 300—270 nm and 270—250 nm have been respectively attributed to the transition from the ground state into the first ($S_0 \rightarrow S_1$), second ($S_0 \rightarrow S_2$) and third ($S_0 \rightarrow S_3$) singlet states. It can be, therefore, supposed that the absorption in the case of PPVK samples occurs also entirely on carbazole groups.

Fig. 1. Transmission of the PPVK and the PVK films in the near uv and visible regions.



The infrared spectra of the PVK and PPVK films are qualitatively similar (see Figs. 2 and 3) and agree very well with the spectra of PVK of other authors [2, 6].

The most intensive absorption bands in their spectra may be attributed to C—H stretching vibrations (around 3000 cm^{-1}) in aliphatic groups, to C=C skeletal vibrations in the aromatic ring (1600 cm^{-1}) and to CH₂ deformation vibrations (around 1450 cm^{-1}). The band structure within 1300 cm^{-1} — 1100 cm^{-1} is most probably caused by C—H in-plane vibrations and around 740 cm^{-1} by a C—H out-of-plane bending in a 1,2-disubstituted aromatic ring [7]. The band at 1705 cm^{-1} was found neither in the spectra of other authors [2, 6] nor in the case of PPVK samples. Its origin may be attributed to C—H stretching in aliphatic groups or C=O stretching caused by impurities in the solution-grown layers.

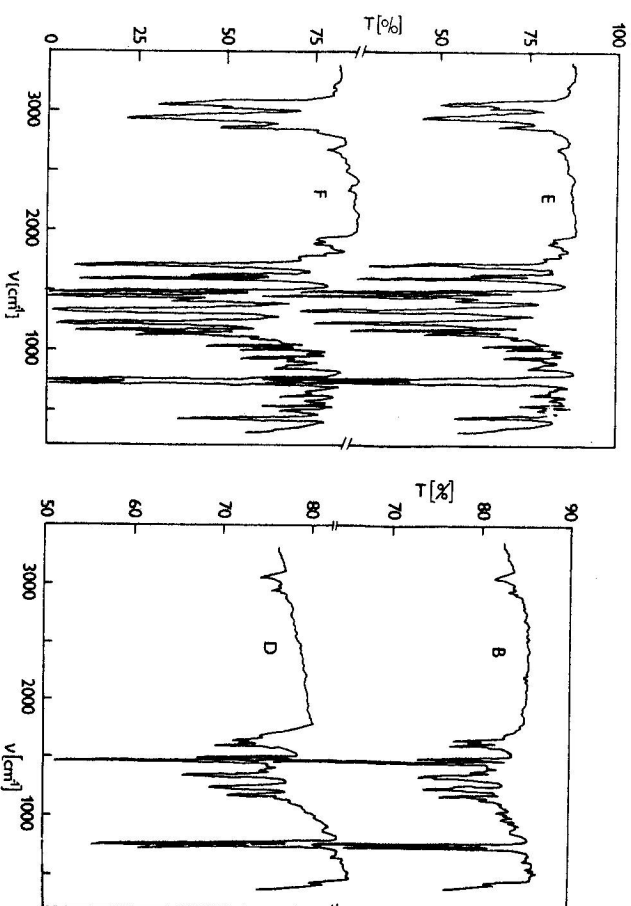


Fig. 2. Infrared spectra of a solution grown PVK (E) and a plasma treated PVK (F)

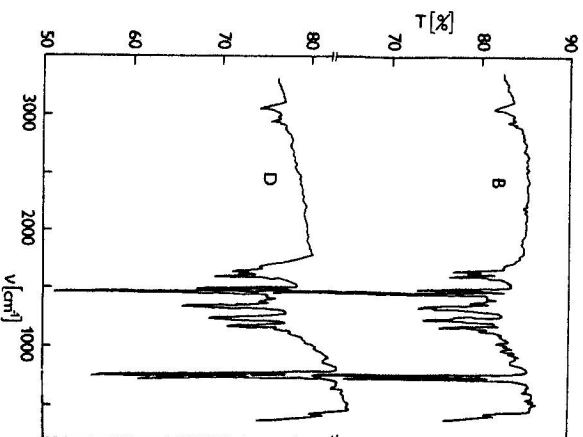


Fig. 3. Infrared spectra of PPVK films.

After the treatment of a PVK sample in the argon discharge (sample F, Fig. 2) the structure became more disordered. A higher increase in the intensity of absorption bands due to C—H vibrations in aliphatic groups (e.g. at

3000 cm^{-1}) with respect to the CH vibrations in aromatic rings documents a partial breaking of the original chemical bonds. On the other hand the absorption band structure of PPVK samples (Fig. 3) is nearly the same irrespective of the power and discharge frequency used.

The ESCA analysis of samples C and E has shown that the surface of PPVK is rather rich in oxygen (the surface concentration of oxygen is comparable with the concentration of nitrogen) whereas the amount of oxygen in PVK is negligible. On the other hand, no oxidation effects have been observed in their spectra. It is, therefore, supposed that the oxygen is bonded only in the surface region after free access of the ambient atmosphere. This effect documents an increased surface reactivity of the plasma, polymerized samples.

IV. CONCLUSION

Although the superstructure of the PVK and PPVK films is expected to be substantially different due to the non-equilibrium process during the plasma deposition, the film characteristics on a molecular level have been found to be very similar for both materials. It is, therefore, very attractive to employ the plasma polymerization process for preparing the layers while the basic film properties are preserved or only slightly different from that of the conventional PVK. This treatment is very promising, e.g., for coating electrographic media [8]. It will be possible to deposit PPVK films with any desired thicknesses (especially very thin) to modify the resulting films by the incorporation of further additives into the growing layers, and to change the film structure and the properties in vacuo during or after the deposition process.

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ТОНКИЕ ПЛЕНКИ ИЗ ПОЛИВИНИЛКАРБАЗОЛА, ПОЛУЧЕННЫЕ ПОЛИМЕРИЗАЦИЕЙ В ПЛАЗМЕ

В работе описано приготовление тонких пленок из поливинилкарбазола методом полимеризации его паров в глущем разряде, возбуждаемом переменным током. Основные структурные характеристики, полученные на основе данных о переходах в ультрафиолетовой, видимой и инфракрасной областях и в результате ESCA-анализа, сравниваются с характеристиками обычных полимеров, полученных из растворов. Обсуждаются возможности применения данных пленок в современной электрографии.