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Properties of the complex salt obtained by doping the poly(*N*-vinylcarbazole) with bromine

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Abstract

Poly(*N*-vinylcarbazole) (PVK) powder has been doped by bromine at room temperature and also at 370, 420 and 470 K for 24–72 h. It is shown, by electron spin resonance (e.s.r.), optical absorption, X-ray photoelectron spectroscopy (XPS), that a charge transfer complex (CT complex) is formed between PVK and Br. However, some bromine is found to react with PVK, even after doping at room temperature, by addition or substitution, since not only bromine anion, which evidences the presence of the charge transfer complex, but also neutral bromine, has been detected by CPS. After heating, our results show that PVK is transformed into a new, more insoluble polymer. This polymer is amorphous, while some traces of carbazole and NH_4Br are present in the powders. The increase of the conductivity is probably related to the formation of some π bonds in the new amorphous polymer. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(*N*-vinylcarbazole); Bromine doping; Complex salt

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1. Introduction

Since the photoconductive properties of the poly(*N*-vinylcarbazole) (PVK) were first shown [1], this polymer has been extensively studied [2,3]. More recently, much attention has been payed to nonlinear optical effects, because it has been shown that organic intracharge transfer compounds should exhibit abnormal large effects.

Nonlinear optical properties of several charge transfer (CT) complex systems have been studied, such as poly(*N*-vinylcarbazole)/2,4,7-trinitrofluorenone (PVK/TNF) [4,5] or acceptor-substituted carbazole derivatives [6]. PVK has also been used as a dopant for poly(3-octylthiophene) in electroluminescent diodes [7].

PVK complex salts have also been studied for xeroradiographic applications [8,9]. Therefore it should be very interesting to study PVK complex salts obtained with halogens. We have shown earlier that the formation of a complex salt with iodine strongly improves the conductivity of the PVK, while a broad absorption appears in the visible domain [10–12]. However, we have shown that it is quite difficult to stabilize the properties of these complex salts by post-annealing treatment, because annealing of PVK under iodine atmosphere induces PVK degradation. In this paper we describe the results obtained after doping PVK with bromine.

2. Experimental

The preparation of powder doped with bromine (purity, 99.99%) was performed as follows: the PVK powder (purity, 99.99%) is introduced, with a small capillary tube full of bromine, in a fused quartz tube previously outgassed. This tube sealed under vacuum was then shaken in order to break the bromine capillary tube. The quartz ampoule was heated at $270\ K < T < 470\ K$ for 24–72 h.

The structure of the different powders was checked by an X-ray diffractometer using an X-ray system-type Diffract AT V3 Siemens instrument which uses a graphics program EVA[1]. The wavelength λ was 1.5406 Å.

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[1] X-ray diffraction measurements were done at the IMN Nantes URA CNRS 110.

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Infrared spectra were obtained with a FT-i.r. spectrometer. Absorption band positions are given in wave numbers (cm^{-1}).

X-ray photoelectron spectroscopy[2] (XPS) measurements were performed with a magnesium X-ray source (1253.6 eV) operating at 10 kV and 10 mA. The energy resolution was 0.75 eV at a pass energy of 50 eV. The samples studied not being very conductive, the powders were fixed to the substrate holder by pressing the polymer powders on a sheet of indium, in order to decrease the charge effect.

The quantitative XPS study was based on the determination of the C1s, N1s, Br3d and O1s peak areas, with 0.2, 0.36, 0.67 and 0.61, respectively, as sensitivity factors (the sensitivity factors were given by the manufacturer (Leybold)). The decomposition of the XPS peaks into different components and the quantitative interpretation, were made after substraction of the background using the Shirley method [13]. The developed curve-fitting programs permit the variation of parameters such as the Gaussian/Lorentzian ratio, the full width at half maximum (FWHM), the position and the intensity of the contribution. These parameters were optimized by the curve-fitting program, in order to obtain the best fit. The binding energy positions were corrected to annul the charging effects. The calibration uses the binding energy of the C1s peak of the hydrocarbon, the position of which is assumed to be constant at 285 eV [14].

The optical measurements were carried out at room temperature using a 'Cary 2300' spectrophotometer. The optical density was measured at wavelengths from 2 to 0.2 μm. Optical measurements were performed on pressed pellets of KBr mixed with a small amount of sample.

E.s.r. experiments were performed at ambient temperature on a Bruker ER 200D spectrometer operating at X band. The decomposition of the e.s.r. spectrum and the interpretation were made using the method described elsewhere [15,16]. Using the pole method integration [17] with a Gaussian or a Lorentzian (or a mixture of the two) line shape, the theoretical e.s.r. signal can be computed yielding parameters of each distribution that can produce the signal after comparison with experimental results.

^{1}H n.m.r. (100 MHz) spectra were recorded on a Varian XL 100 spectrometer. TMS was used as the internal standard and $CDCl_3CD_3$–CO–CD_3 as solvent, and lock.

In order to check the results obtained by ^{1}H n.m.r., mass spectrometry was performed with a Bruker 250 WM spectrometer. The dc conductivity measurements were performed at room temperature with an electrometer (Keithley) on pressed pellets (thickness 0.5 mm, diameter Ø = 12 mm). The two faces of the pellets were metallized by evaporation of gold wire under vacuum. Copper wires were stuck by silver paste on to the golden faces of the pellets.

3. Experimental results

The powders were doped under different conditions: doping at room temperature, 370, 430 and 470 K for 1 to 3 days, they were then systematically studied by optical absorption (i.r. and visible), X-ray electron spectroscopy (XPS), electron spin resonance (e.s.r.), nuclear magnetic resonance (n.m.r.) and conductivity measurements.

3.1. Optical absorption

I.r. spectra are presented in Fig. 1. It can be seen that no modification occurs in the i.r. spectra of PVK after bromine doping at room temperature (Fig. 1b) or at 370 K (Fig. 1c). When the doping temperature increases, first the FWHM of the peak increases (Fig. 1d), while for higher temperature the wave number of the absorption peaks is modified. The intensity of some peaks decreases while new peaks appear (Fig. 1e,f). To help the discussion, the i.r. spectrum of the carbazole powder is also reported Fig. 1g.

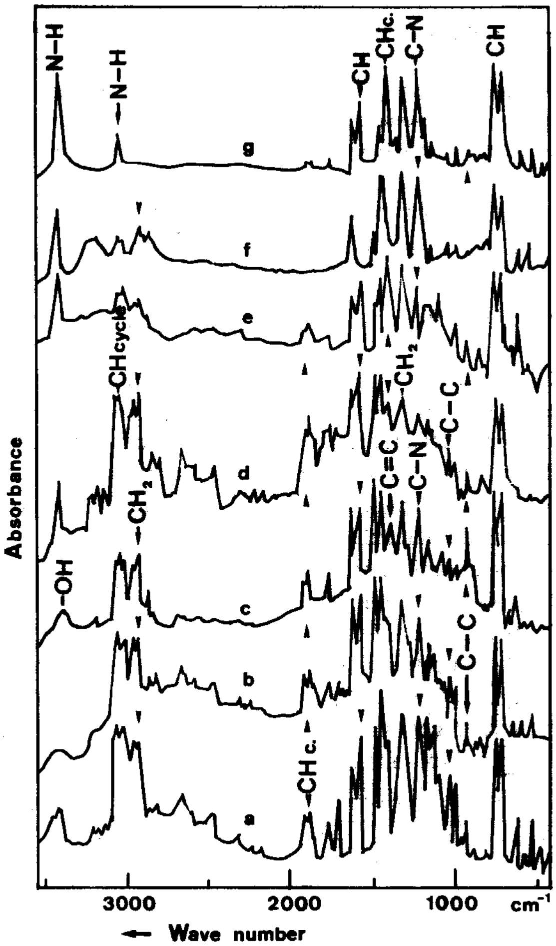

Fig. 1. I.r. spectra: (a) pure PVK powder; PVK powder dope with bromine at (b) room temperature; (c) 370 K for 24 h; (d) 420 K for 24 h; (e) 470 K for 24 h; (f) 470 K for 24 h 3 months later; (g) carbazole powder.

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[2] XPS measurements were done with a Leybold apparatus (University of Nantes—CNRS).

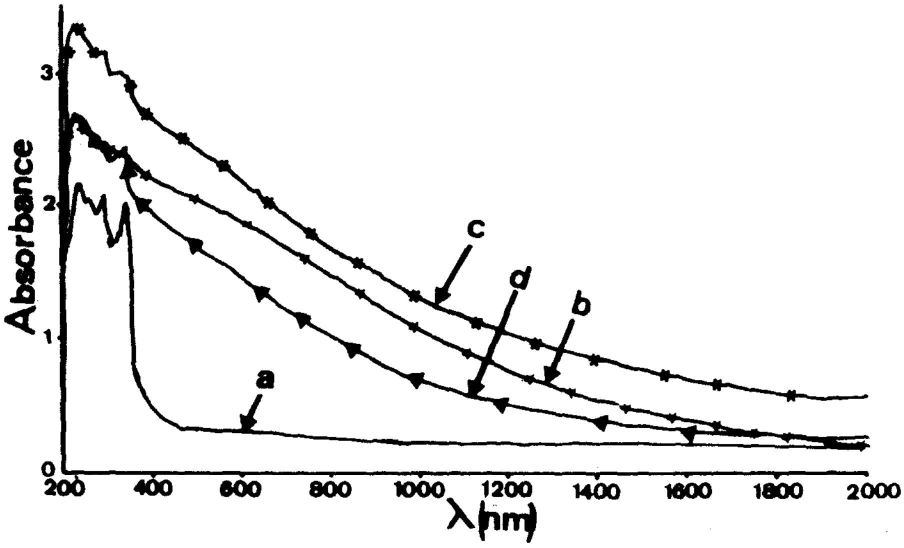

Fig. 2. Visible absorption spectra: (a) pure PVK powder; PVK powder doped with bromine at (b) 270 K for 24 h; (c) 420 K for 24 h; (d) 470 K for 24 h.

The optical absorption[3] spectra are reported in Fig. 2. It can be seen that a large absorption band appears from 400 to 1000 nm (Fig. 2b–d) while the features corresponding to pure PVK (Fig. 2a) are always present after an annealing of 24 h at 470 K.

3.2. XPS analysis

Various curves are shown in Fig. 3. Quantitative analysis indicates that 5–10 at.% of bromine is present whatever the temperature of doping. The different peaks have been decomposed into different contributions (Table 1).

The C1s spectrum (Fig. 3a) is skewed towards the high energy side with the main component taken as reference at 285 eV. This peak is used as the reference for the other binding energies since this value corresponds to the well-known hydrocarbon binding energy. The second peak can be attributed to C–N bonds, since it is situated at 286 eV [18]. It can also be partly attributed to $C^{\delta+}$ radicals. Two other peaks can be obtained from the decomposition of the tail. The component located at about 287.4 eV can be attributed to hydroxyl bonds, while the other one situated at about 289.2 eV can be attributed to carbonyl bonds. The N1s peak exhibits (Fig. 3b) a shoulder in the high binding energy side and therefore it should decompose into two components. The main one located at 400.6 eV corresponds to the carbazole unit, while the other one located at higher energy corresponds to positively charged nitrogen $N^{\delta+}$. Additional information concerning the oxidation process can be obtained from Br3d (Fig. 3c) and the O1s peaks (Fig. 3d). After doping at 470 K, the width of the Br3d peak, which is a doublet, is broader than the expected value. Therefore, one may expect this structure to originate from two different doublets superimposed in such a way that the peak located at the smallest binding energy corresponds to the ionic state of bromine Br^-, while the other one is due to covalently bonded bromine. In the case of the doping at room temperature, the atomic percentage of ionic bromine is smaller (Table 1).

The O1s peak can be also decomposed into two components, the first one at about 531.7 eV is attributed to C=O and the higher energy peak at 533.7 eV corresponds to C–O–H groups.

3.3. XRD study

The XRD spectra obtained with different powders are presented in Fig. 4. The spectrum of the powder doped at room temperature (Fig. 4a) is similar to that of the pure powder. After doping at 380 or 420 K (Fig. 4b,c) the large peak situated at about $2\theta = 20°$ increases. When the doping temperature is increased ($T = 470$ K, Fig. 4d) some other new peaks appear for $d = 0.597$ Å, $d = 4.446$ Å, $d = 3.795$ Å and $d = 3.156$ Å.

The intensity of the new peaks increases when the annealing time increases from 1 to 3 days (Fig. 4e). Here also, the XRD spectrum of reference of the carbazole powder is reported (Fig. 4f).

3.4. N.m.r. experiments and mass spectrometry

The powders are dissolved in $CDCl_3$. However, the solubility of the powders decreases as the annealing temperature increases and longer acquisition times were needed to obtain resolved spectrum. Under the acquisition conditions used even impurity traces such as $CHCl_3$, acetone used for cleaning the glass tube containing the sample, etc., are detected (Fig. 5). The broad peaks of the ^1H n.m.r. spectrum of Fig. 5a is attributed to PVK.

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[3] Optical measurements were done at the LPC-IMN Nantes URA CNRS 110.

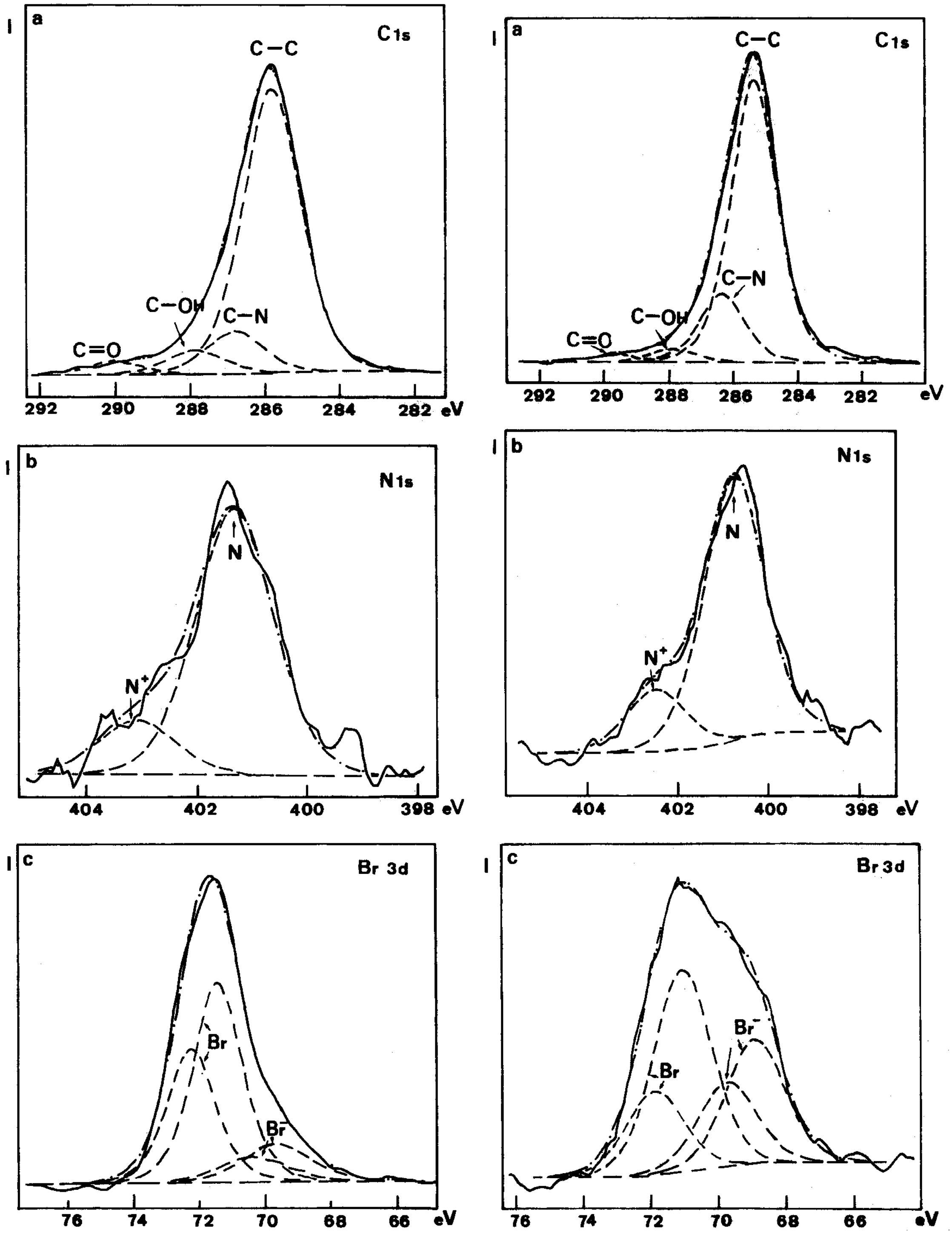


Fig. 3. XPS spectra of the (a) C1s, (b) N1s, (c) Br and (d) O1s peaks: (1) after doping with bromine at room temperature; (2) after doping with bromine at 470 K for 24 h. (——) Experimental data; (– · –) theoretical curve; (— — —) different components.

After doping with bromine at 370 or 420 K for 24 h (Fig. 5b,c), some part of the material had become insoluble and therefore could not be analysed by n.m.r., and the peaks attributed to PVK had disappeared. Some new features, attributed to some carbazole oligomers, appeared [11], whereas a new strong peak attributed to NH_4Br appeared at about $\delta = 2.85$ ppm (Fig. 5d,e). These results are amplified with the increase of the doping temperature and when the doping at 420 K is applied for 3 days (Fig. 5e). Furthermore, while no PVK could by solubilized from the powders using $CDCl_3$ as solvent, subsequent extraction with D6-acetone gave the ^1H n.m.r. spectra (Fig. 5d,e). The comparison of these with the pure carbazole one (Fig. 5f) shows that they are identical. These results have been checked by

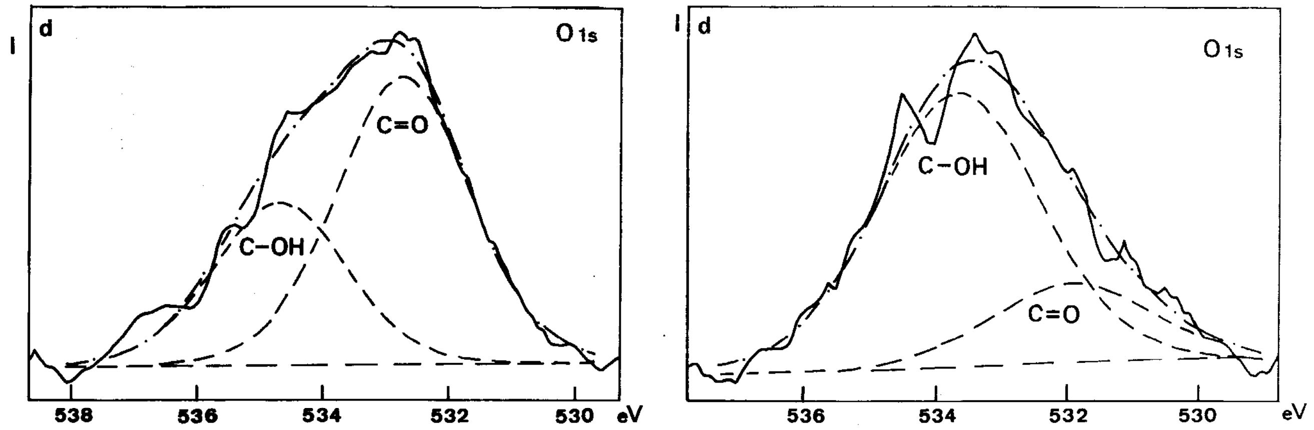


Fig. 3. Continued.

mass spectrometry, two masses 168 and 169 confirm the presence of carbazole monomer (M and MH^+).

3.5. *E.s.r. and conductivity measurements*

No e.s.r. signal is observed for pure PVK powder before doping. After doping, a well-resolved e.s.r. signal is systematically observed at 300 K. The e.s.r. spectra of doped samples are shown in Fig. 6. In order to facilitate the comparison of g factors and of full width at half maximum (FWHM), the spectra have been normalized to a constant height (Fig. 6). As can be seen, the shape of the signal depends on the doping conditions. After doping during 24 h at room temperature or at 420 K the signal is not symmetrical while it is at 470 K. The accordance between experimental and theoretical curves can be obtained: (a) in the case of doping at room temperature when two isotropic Zeeman distributions are used (Table 2 and Fig. 7a); (b) in the case of doping at 420 K we must use three axial Zeeman distributions (Table 2 and Fig. 7b); (c) in the case of doping at 470 K only one isotropic Zeeman distribution is used (Table 2 and Fig. 7c).

We should note that the more complex situation occurs at 420 K, but if we compare the g_{iso} values of the D′2 and D′3 distributions, they seem to be derived from the D1 and D2 distributions observed for the doping at room temperature, which will be discussed later.

After doping at room temperature only a slight increase of room temperature conductivity is observed; however, the effect of bromine doping increases with doping temperature (Table 3).

4. Discussion

The results of the infrared absorption, n.m.r., XRD, and XPS measurements have shown that, after doping at room temperature with bromine, the PVK powder properties are quite similar to those of the pure powder, which means that the main properties of the polymer chains are preserved. However, the modification of the optical density, the appearance of an e.s.r. signal, and the presence of Br^- as shown by XPS, indicates the formation of some complex salt between the PVK and the bromine. The large new absorption band between 400 and 1000 nm in the optical density spectrum is typical of charge transfer complex

Table 1
XPS analysis of PVK powder, pure or doped with bromine

	C1s				N1s		O1s		Br	
	C–C	(C+) C–N	C–O–H	C=O	N	N^+	O_x		Br^-	Br
							C=O	C–O–H		
Pure PVK ($\Delta E = 1$ eV)	285	286.5			400.4	—			—	—
	73	27								
PVK doped with Br for 24 h at room temperature ($\Delta E = 0.8$)	285	286	287.1	289.2	400.6	402.3	531.9	533.8	68.8	70.7
	78	12	6.5	3.5	83	17	64	36	20	20
PVK doped with Br at 470 K for 24 h ($\Delta E = 0.3$)	285	286	287.5	289.3	400.7	402.5	531.6	533.7	68.9	71
	76	18	4	2	81	19	22	78	40	60

First line, binding energy (eV); second line, at%. ΔE is the charge effect (i.e. the binding energy difference between the measured value for C1s and the value taken as reference: C1s = 285 eV)[18]

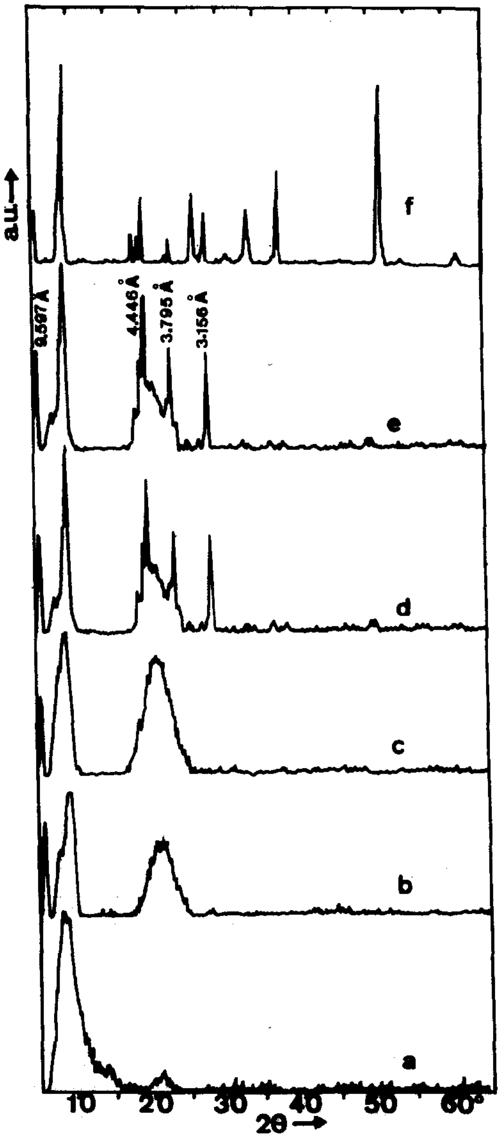


Fig. 4. XRD spectra: PVK powder doped at: (a) room temperature; (b) 370 K for 24 h; (c) 420 K for 24 h; (d) 470 K for 24 h; (e) 470 K for 3 days; (f) carbazole powder.

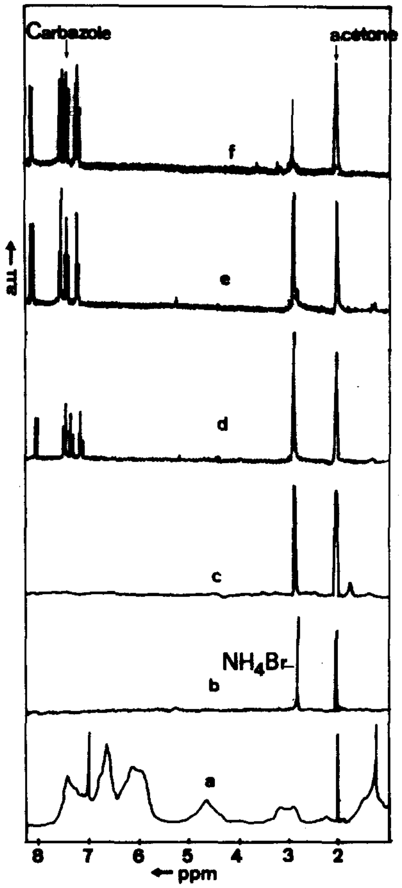
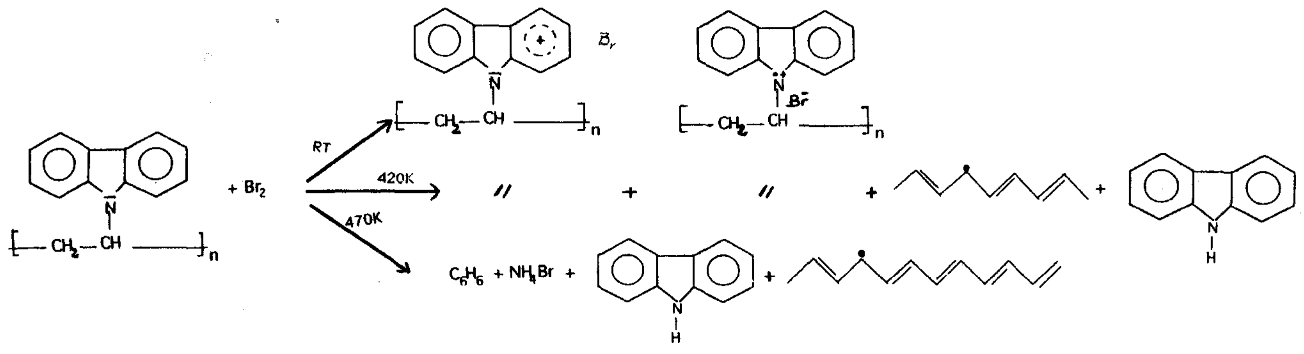


Fig. 5. N.m.r. spectra: PVK powder doped at: (a) room temperature; (b) 370 K for 24 h; (c) 420 K for 24 h; (d) 470 K for 24 h; (e) 470 K during 3 days; (f) carbazole powder.

formation. Also the e.s.r. signals (Fig. 6) can be attributed to formation of radicals. The origin of spins is the charge transfer complex formation between PVK and bromine. The carriers so formed are localized on the carbazole units since only σ bonds are present in the aliphatic chains (Scheme 1). Since D1 is 2.0090 and D2 is 2.0026 these radicals can correspond to $N^{\delta+}$ and $C^{\delta+}$ detected by XPS. The $N^{+}1s$ signal can also be attributed to nitrogen bonded to bromine since it has been shown by XPS that two different chemical states of bromine coexist in the doped PVK



Scheme 1.

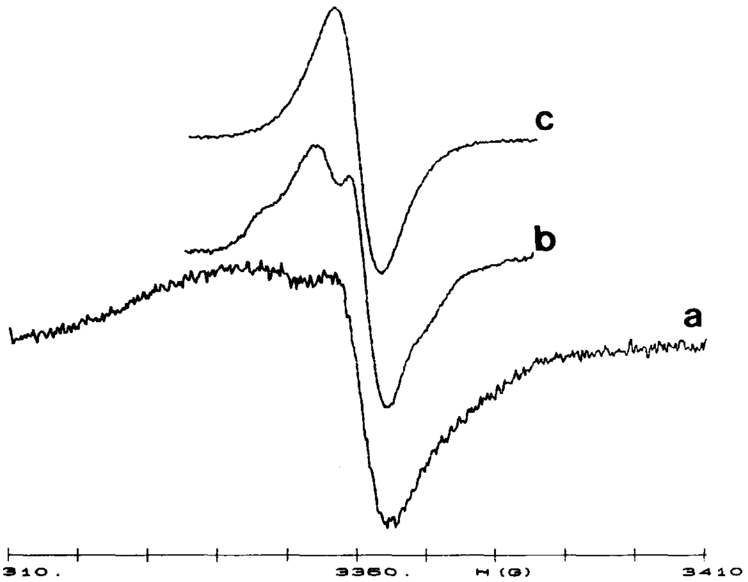


Fig. 6. E.s.r. spectra: PVK powder doped at (a) room temperature for 24 h; (b) 420 K for 24 h; (c) 470 K for 24 h.

powder, and since the n.m.r. studies reveal the presence of NH_4Br (Fig. 5b–e).

After doping at room temperature, the room temperature conductivity increases ($4 \times 10^{-9}\,\Omega^{-1}\,cm^{-1}$ after doping, compared to 10^{-14} to $10^{-17}\,\Omega^{-1}\,cm^{-1}$ before doping). However, the conductivity of the doped polymer is small because the carriers are localized on carbazole units since the aliphatic chain is saturated with only σ bonds (Scheme 1). The results are quite different after doping at higher temperature. The signals related to PVK which either disappear (XRD, n.m.r.) or are strongly modified (i.r., e.s.r.) indicate a degradation of the polymer.

It has been shown earlier [19,20] that the narrow peak situated at $2\theta = 8°4'$ can be attributed to the crystallized PVK phase, while the broad one situated at 21°5′ corresponds to the disordered phase. Therefore, since the intensity of this last peak increases after doping at a temperature higher than the room temperature, we can conclude that the disorder increases in the polymer. By comparison to the reference spectrum of the carbazole monomer in Fig. 4f, and to the JCPDS data [21], the new peaks which appear in the XRD spectra should be attributed to carbazole. The progressive degradation of the PVK induces formation of a carbazole crystal embedded in an amorphous polymeric matrix. This new polymer becomes progressively insoluble as stated during n.m.r. experiments.

The only phases which are soluble, in chloroform and acetin, as shown by n.m.r., are the carbazole monomer and the NH_4Br. However, it can be seen from Fig. 5 that these compounds are only present as traces in the polymer, since the signal intensity of these phases is of the same order of magnitude as that of the impurities present in the glass tube containing the sample. Since it has become insoluble after bromine doping, the main part of the polymer cannot be analysed by n.m.r.

The modification of the polymer and the appearance of carbazole monomer units is confirmed by i.r. measurements (Fig. 1), since not only vibration frequencies are modified which shows that new bonds are present in the polymer, but also some typical peaks of carbazole monomers appear in the spectrum (N–H, 3420 cm^{-1}; C–N, 1230 cm^{-1}), while some others, typical of poly(*N*-vinylcarbazole), decrease strongly: aromatic cycle (3048, 1918, 1888 cm^{-1},...); CH_2 (2963, 2929 cm^{-1}...). In the literature [22] the vibrations corresponding to C=C bonds are situated between 1200 and 1600 cm^{-1}. After bromine doping at 370 K (Fig. 1c), or more (Fig. 1d), a well-resolved absorption band appears at 1400 cm^{-1}, which could be attributed to C=C bonds.

The progressive degradation of PVK increases with annealing temperature during doping. An interesting result is given by an e.s.r. study. Figs 6 and 7 and Tables 2 and 3 show that the e.s.r. signal and room temperature conductivity are modified by the annealing temperature.

After doping at 420 K three distributions (Table 2) are necessary to obtain the experimental and theoretical curves fitted together. The reaction between Br and PVK induces strong modifications of the initial powder. Bromine can break the N–C bonds, resulting in carbon chains and carbazole formation. The new radical should be located on the carbon chains (Scheme 2). In addition, a new amorphous reticulated matrix appears. This amorphous matrix, which is strongly disordered, is composed of C–C bonds (σ bonds) but also of C=C bonds (π bonds). The formation of NH_4Br is in agreement with e.s.r. results, as we can see, the relative intensity of the D′3 distributions is strongly reduced.

A value of $g_{iso} = 2.0073$ can be taken from the D1 distributions observed for the room temperature doping attributed at $N^{\delta+}$ radical. We note also a partial destruction of the polymer and D′1 distribution ($g_{iso} = 2.0022$) agree with this assumption. At 470 K the signal is only constituted

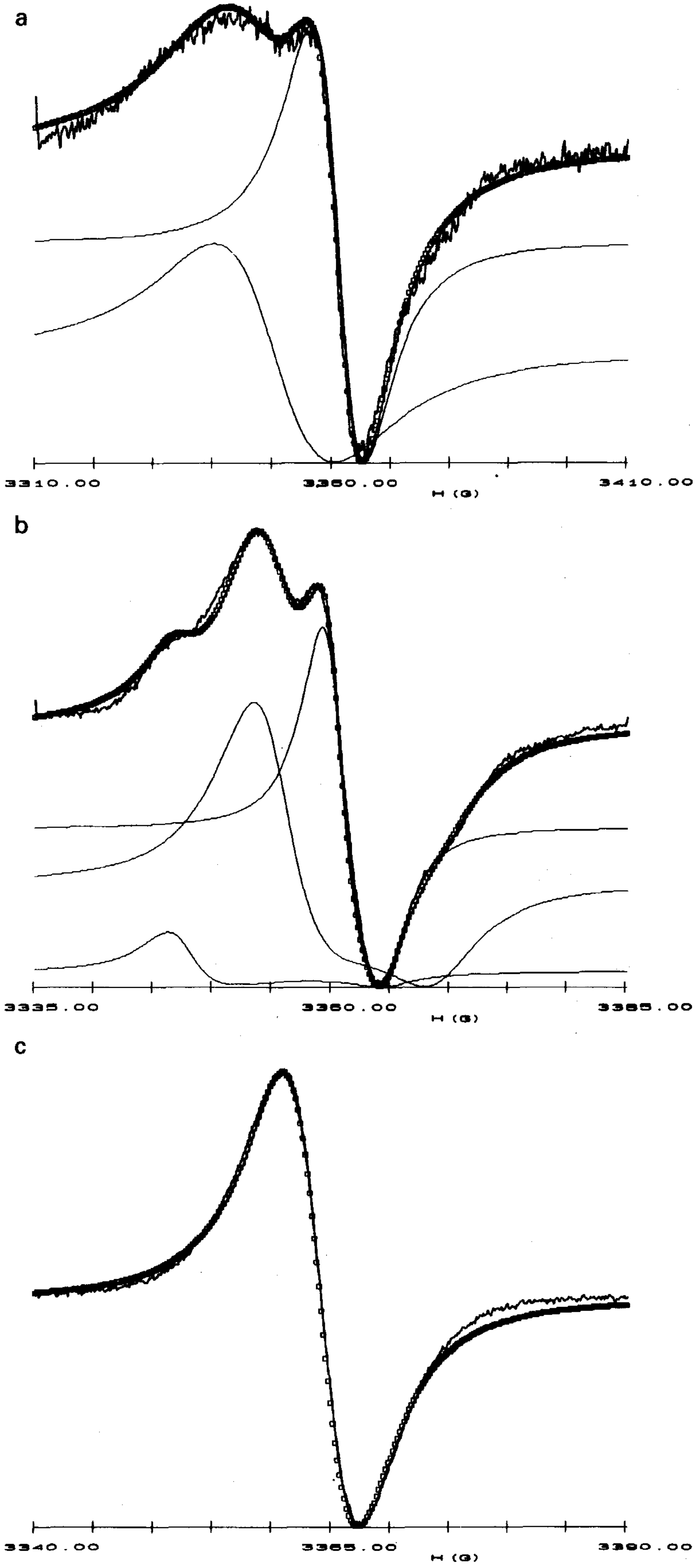

a
3310.00
3360.00
H (G)
3410.00
b
3335.00
3360.00
H (G)
3385.00
c
3340.00
3365.00
H (G)
3390.00

Table 2
Results of ESR analysis of the PVK doped with bromine as function of treatment temperature

Sample PVK powder doped with bromine		g_{xy}	g_z	g^a_{iso}	Width^b (G)	Irel (%)^c
At room temperature	D1	—	—	2.0090 (1)	20.0 (2)	50 (1)
	D2	—	—	2.0026 (1)	9.0 (2)	50 (1)
At 420 K for 24 h	D′1	2.0031 (1)	2.0005 (1)	2.0022 (3)*	3.0 (2)	41 (1)
	D′2	2.0061 (1)	1.9980 (1)	2.0042 (3)*	5.5 (2)	46 (1)
	D′3	2.0107 (1)	2.0005 (1)	2.0073 (3)*	4.0 (2)	13 (1)
At 470 K for 24 h	D″1	-	—	2.0028 (1)	6.4 (2)	100

$^a g_{iso} = (2g^2_{xy} + g^2_z)^{1/2}$
^{b}The width is given for a Lorentzian shape of line
^{c}Relative contribution of the component to the whole signal

by one distribution similar to the D′1 observed at 420 K, and we can imagine that total destruction of the PVK polymer is achieved and this e.s.r. signal can be attributed to the amorphous polymer matrix (Scheme 3).

The room temperature conductivity of a room temperature doped polymer increases ($10^{-9}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ compared to 10^{-14} to $10^{-17}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ before doping) because of the charge exchange between the PVK and Br. However, the conductivity of the doped PVK is small because the carriers are localized on carbazole units since the aliphatic chain is saturated with only σ bonds. After heating during doping, the conductivity increases because of the degradation of the PVK and the formation of a new polymer with partly conjugated chains and radicals. The π bonds allow the increase of the conductivity since the carriers evidenced by e.s.r. are able to move along these conjugated chains, the hopping process being needed only to jump from one conjugated chain to another one. It should be noted that the bromine concentration present in polymer is independent of the doping temperature. The percentage of ionic bromine is only 20 at% after doping at room temperature, while it is 40 at.% after doping at 470 K. This result is in good agreement with the increases of the intensity of the e.s.r. signal and of the conductivity.

5. Conclusion

A CT-complex between PVK and bromine has been obtained after bromine doping of PVK at room temperature, as shown by optical density, e.s.r. and XPS measurements. However, the high electronegativity of bromine and the fact that the aliphatic chains of PVK is saturated induces strong localisation of the carriers.

Moreover, a large part of bromine has reacted with the PVK. When the doping is carried out at a temperature above the room temperature the PVK is decomposed with formation of a carbazole monomer imbedded in a new amorphous polymer. The conductivity of this new polymer is higher than that of doped PVK, probably due to the formation of π bonds induced by crosslinking between the chains.

Table 3
Comparison of ESR spin intensity and room temperature conductivity measurements

Sample of PVK powder doped with bromine	ESR intensity, I/I_0	Electrical conductivity, $\sigma(\Omega\ \mathrm{cm})^{-1}$
Pure PVK	0	10^{-4} to 10^{-17}
At room temperature	1	10^{-9}
At 420 K for 24 h	1.7	10^{-7}
At 470 K for 24 h	6.1	10^{-4}

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Fig. 7. E.s.r. signal decomposition: PVK powder doped at (a) room temperature for 24 h; (b) 420 K for 24 h; (c) 470 K for 24 h. Jagged line, experimental data: (– □ –) theoretical curve; (——) different components.