Study of the Evolution of the Conductivity of Iodine-Doped Poly(N-Vinylcarbazole) as a Function of Annealing Treatment

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SYNOPSIS

Electron spin resonance (ESR) and d.c. conductivity measurements on iodine-doped poly(N-vinylcarbazole) (PVK) as a function of annealing treatment was performed. When doped at room temperature as at 370 K, the appearance of an ESR signal and the increase of the conductivity can be explained by CT complex formation between iodine and PVK. The correlation between conductivity σ and spin density N_S was observed as a function of the annealing temperature. At higher annealing temperature, the decrease of the conductivity and of the ESR signal is attributed to the PVK degradation and to the formation of a new conjugated polymer. All these results and their discussion are in good agreement with X-ray diffraction, Raman diffusion, and earlier studies. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In our previous studies[1,2], we showed that annealing of poly(N-vinyl carbazole) under iodine pressure induces a progressive polymer degradation. Infrared absorption, X-ray photoelectron spectroscopy, X-ray diffraction, and nuclear magnetic resonance have shown[1,2] that when the annealing temperature is higher than 370 K there is a progressive partial graphitization of the polymer. At the end of the process, for an annealing at 570 K, 24 h under iodine pressure, the powder is composed of small NH_4I crystallites imbedded in an amorphous matrix of a new polymer. To have the best understanding of the chemical decomposition process, we pursued our study by doing electron spin resonance (ESR) and conductivity (σ) measurements. After a brief recalling of the doping technique used and of the experimental techniques, the results are described and extensively discussed. It is shown that ESR and σ measurements are in close agreement. The evolution of the ESR signal follows that of the conductivity. The evolution of the conductivity of the polymer after annealing is attributed to the modification of the polymer, which is in good accordance with X-ray diffraction (XRD) and Raman diffusion studies.

EXPERIMENTAL

The poly(N-vinylcarbazole) was provided by Aldrich; its purity was 99.99%. The iodine-doping process used was that described by Gutierrez.[3] It was described more extensively earlier[1] and the annealing process also. In this work, three annealing temperatures were used: 370, 470, and 570 K. The annealing time was 24 h, under iodine pressure. We have shown[1] by X-ray photoelectron spectroscopy (XPS) that in each powder there is only $\approx$ 3 at. % of iodine. ESR experiments were performed at ambient temperature on a Bruker ER 200 D spectrometer operating at the X band. Spin density N_S was estimated using an ESR comparison technique. The minimal sensitivity of the detector is $\approx 10^{15}$ spins cm^{-3} mol^{-1}. The decomposition of the ESR spectrum and the interpretation was made using the method described elsewhere.[4,5] Using the pole method integration[6] with a Gaussian or a Lorentzian (or a mixture of two) line shape, the theoretical ESR signal can be computed yielding parameters of each
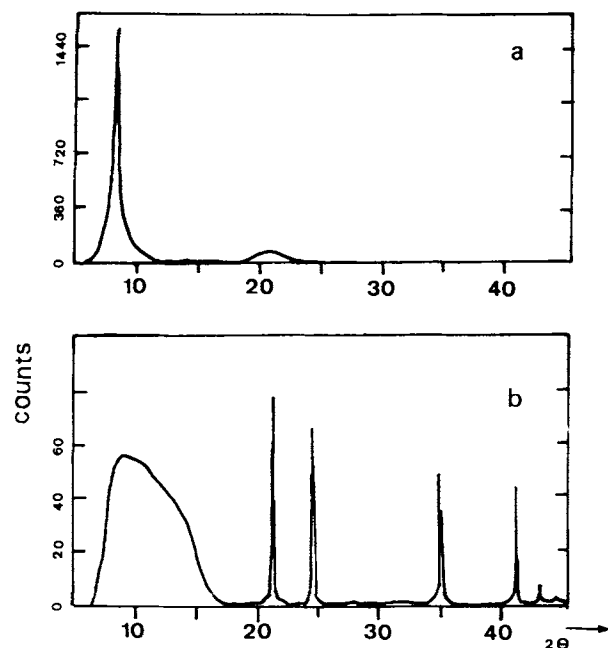
Figure 1 XRD spectra of some PVK: (a) pure powder annealed at 570 K; (b) powder annealed at 570 K under iodine atmosphere.

distribution that can produce the signal after comparison to experimental results. The conductivity of the samples was measured on powder pellets pressed at $5 \cdot 10^6$ Pa. The two faces of the pellets (diameter $\phi = 8$ mm) were metallized by evaporation of gold wire under a vacuum. Copper wires were stuck by silver paste on the goldened faces of the pellets. An electrometer (Keithley 617) was used to measure the d.c. conductance between 290 and 440 K. The limited temperature domain was due to the quite high resistivity of some pellets for the low-temperature limit and to the polymer degradation for the high-temperature limit.

The structure of the powders was examinated with an analytical X-ray system, type Diffract AT V 3.1 Siemens, which uses the graphics program EVA. The wave length λ was 1.5406 Å with the CuKα source. The structure of the samples was also examined by Raman diffusion. For the Raman experiments, the apparatus used laser excitation with the wavelength $\lambda = 1064$ nm. The laser power and the scale number necessary to obtain a good signal-to-noise ratio were 100 mW and 400, respectively.

RESULTS

XRD and Raman Diffusion Studies

The XRD spectra obtained with the different powders are presented in Figure 1. After annealing of
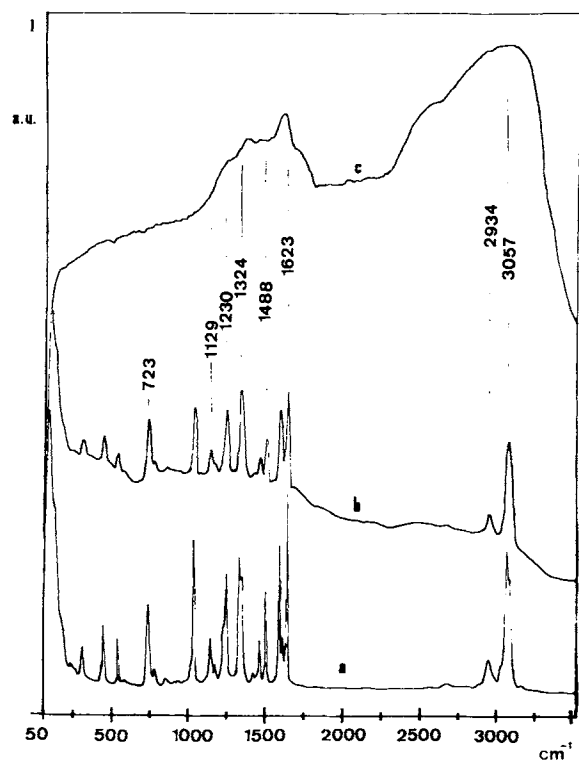

Figure 2 Raman spectra of PVK: (a) pure PVK powder; (b) room temperature iodine-doped powder; (c) iodine-doped powder at 473 K.

the pure powder PVK at 570 K, the spectrum exhibits [Fig. 1(a)] the two classical peaks expected in PVK at $2\theta = 8.4°$ and $2\theta = 21.5°$.[2,7,8] After annealing at $T \geq 470$ K under an iodine atmosphere, while the PVK spectrum disappears, new peaks appear in the XRD spectrum [Fig. 1(b)]. These new peaks have a very small intensity but they are always the same and they are very well resolved. They can be attributed to NH_4I.[9]

To check the degradation process, we proceeded to Raman diffusion experiments. The spectrum of

Table I   Main Raman Bands

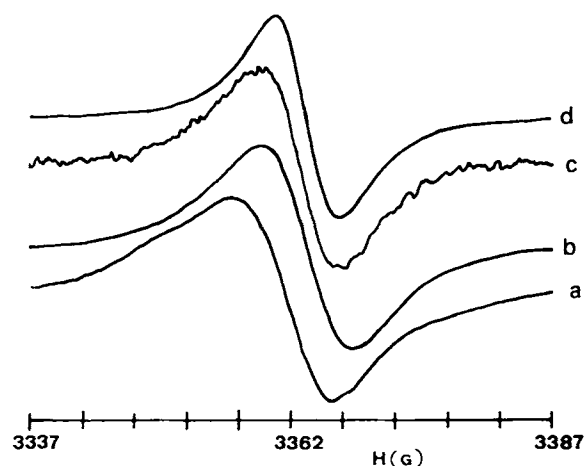| Frequency ν (cm^{-1})	Vibration
3057	C—H aromatic
2934	CH$_2$ antisymmetric stretch
1623	Symmetric C=C
1488	Ring stretch
1324	Ring vibration
	C$_{aromatic}$—N
1230	Ring vibration
1020	Ring vibration
723	Ring vibration
431	C$_3$—N

Figure 3 Normalized ESR spectra of PVK doped with iodine: (a) at room temperature; (b) at 370 K under iodine pressure; (c) at 470 K under iodine pressure; (d) at 570 K under iodine pressure.

the reference PVK powder is reported Figure 2(a). The main absorption bands are attributed in Table I. It can be seen in Figure 2(b) that after iodine doping at room temperature the spectrum is nearly the same. However, after doping at 473 K, the spectrum is strongly modified. The large band around 3000 cm^{-1} is typical of a deteriorated polymer. Even in the domain composed between 300 and 1700 cm^{-1}, the bands are very poorly resolved. The wide bands can be attributed to the loss of translational symmetry[10] related to the degradation of the polymer during annealing under iodine atmosphere. The bands related to N bonds have nearly disappeared.

ESR Measurements

No ESR signal was observed before doping. After doping, a well-resolved ESR signal is systematically observed. The ESR spectra of doped samples are

shown in Figure 3. To facilitate the comparison of the g factors, the spectra were normalized to constant height. The spectrum of the PVK powder doped with iodine at room temperature [Fig. 3(a)] is quite different from the others [Fig. 3(b), (c), and (d)]. It can be seen (Table II) that ΔH_{pp} decreases when the annealing temperature increases. The ESR signal is nearly stable up to an annealing at $T = 370$ K; then, there is a strong increase of the signal with a maximum for $T = 470$ K as the annealing temperature.

With the ESR spectrum of the powder doped with iodine at room temperature being quite different from the others (Fig. 3), we will first discuss it. If only one isotropic g is used, the best result is obtained when $g_x = g_y = g_z = 2.000$ and $\Delta H_{pp} = 9G$; however, as can be seen [Fig. 4(a)], the accordance between experimental and theoretical curves is very poor. The same discrepancy is obtained when two g isotropics are used ($g_x = g_y = g_z = 2.000$; $\Delta H_{pp} = 9G$ and $g_{1x} = g_{1y} = g_{1z} = 2.004(5)$; $\Delta H_{pp} = 6G$) [Fig. 4(b)]. A far better fit is obtained [Fig. 4(c)] using an anisotropic ESR signal, with $g_x = g_y = 1.998(7)$, $g_z = 2.004(3)$, and $\Delta H_{pp} = 8G$. The radicals can be attributed to the nitrogen of the carbazol units.[11] The signal anisotropy of the PVK powder doped at room temperature by iodine could be attributed to the radical environment (Scheme 1), since at this temperature, there is no degradation of the polymer as shown by IR and XRD measurement.[1,2] This anisotropy is not unexpected in polycrystalline powder.[4]

After annealing, the ESR signal can be easily fitted with a symmetrical g (Table II, Fig. 5). Figure 5 shows the spectrum of the PVK powder doped at 570 K. It can be seen that a good correlation is obtained between the experimental and calculated spectra. The g values, width of the signal ΔH_{pp}, and the spin density (N_S) are reported in Table II.

Table II   XPS, ESR, and Conductivity with the Annealing Conditions as a Parameter

| PVK Powder	XPS Iodine at %	ESR g	ΔH_{pp} (Gauss)	N_S: Spin Density (cm^{-3} mol^{-1})	Conductivity σ at 300 K (Ω cm)$^{-1}$	E_a (eV)
Doped at room temperature	2	$g_x = g_y = 1.998(7)$ $g_z = 2.004(3)$	8.00	$2.5 \cdot 10^{17}$	$2 \cdot 10^{-13}$	0.5
Annealed at $T = 370$ K under iodine pressure	3	$g = 1.998(8)$	8.50	$2 \cdot 10^{17}$	$2 \cdot 10^{-13}$	0.7
Annealed at $T = 470$ K under iodine pressure	3	$g = 1.999(1)$	7.40	$5 \cdot 10^{18}$	$1 \cdot 10^{-6}$	0.1
Annealed at $T = 570$ K under iodine pressure	3	$g = 1.998(8)$	7.20	$2 \cdot 10^{18}$	$2.5 \cdot 10^{-8}$	0.15
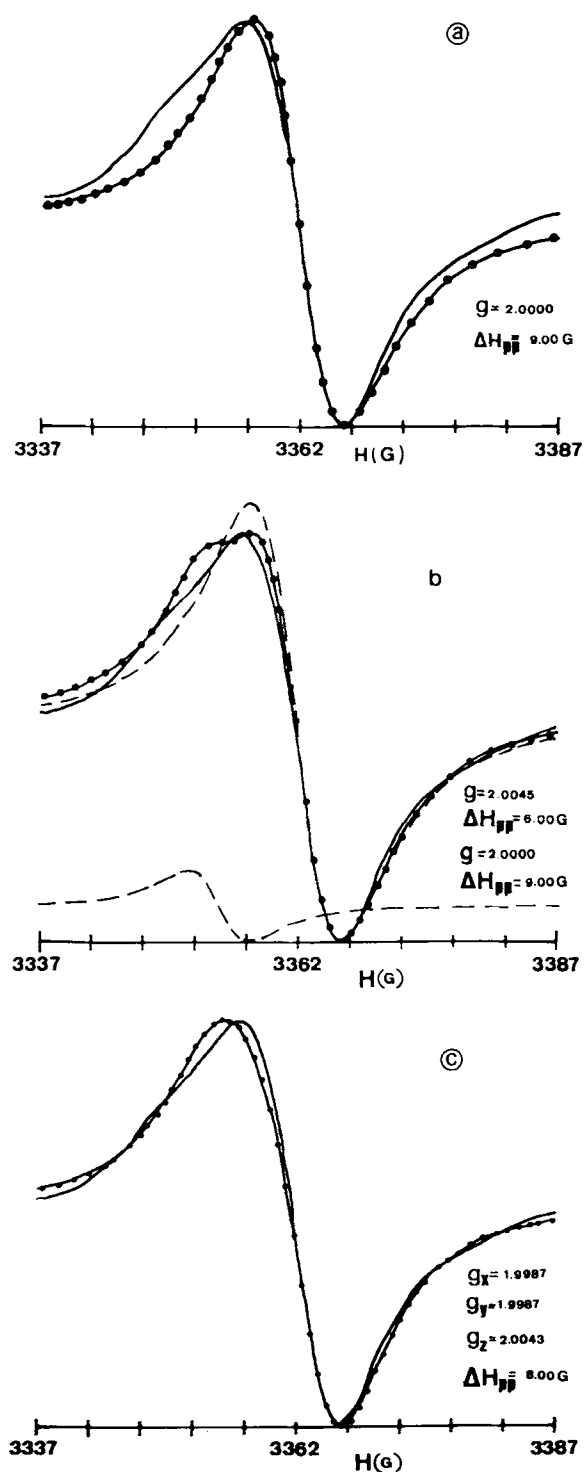
Figure 4 Comparison of ESR spectrum for PVK powder doped with iodine at room temperature with theoretical spectrum: (a) Experimental spectrum, computed simulated ESR spectrum for isotropic signal; (b) Experimental spectrum, computed simulated sum ESR spectrum of two isotropic signals, computed simulated decomposition ESR spectrum; (c) Experimental spectrum, computed simulated ESR spectrum for anisotropic signal which represents the best fit to the experimental spectrum.
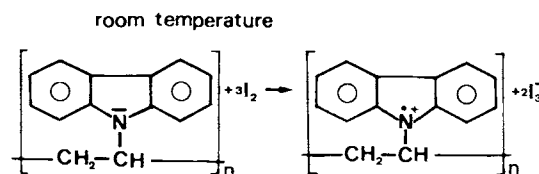
Scheme 1.

It can be concluded that, after annealing ($T \geq 370$ K) of the PVK powder under an iodine atmosphere, the environment of the radical is modified, which means that there is some modification of the polymer. We have already shown[1] that for annealing at $T = 370$ K the chain length decreases. At higher temperature, there is polymer degradation as shown by XRD (Fig. 1). Iodine can break the N—C bonds and there is also NH_4I formation [eq. 1, Scheme 2), while radicals can be situated in the carbon chains:

$$(C_{14}NH_{11})_n + \frac{n}{2} I_2 \rightarrow nNH_4I + (C_{14}H_7)_n \quad (1)$$
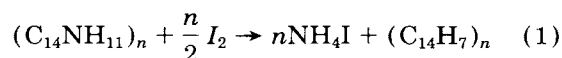
For annealing of the PVK powder under iodine atmosphere at 570 K, the degradation of the polymer is completed with NH_4I microcrystals [Fig. 1(b)] embedded in an amorphous matrix polymer. This polymer being reticulated as proposed in Scheme 3.

Conductivity Measurements

Figure 6 shows the variation of the conductivity with reciprocal temperature. The room-temperature conductivities σ and the activation energies E_a deduced from the Arrhenius plots are reported in Table II. We note that the samples can be divided into two classes:

- The samples not annealed or annealed at low temperature ($T \leq 370$ K) are quite resistive and they have a great activation energy.
- The samples annealed at high temperature (470 or 570 K) have a smaller activation energy and a larger conductivity. The conductivity increases by, at least, five orders of magnitude (Table II). This increasing of σ cannot be attributed to crystallization because, earlier, we showed[2] that powder is amorphous after iodine doping at these temperatures.

DISCUSSION

We have shown by XRD and Raman measurements that after annealing of the PVK powder under an
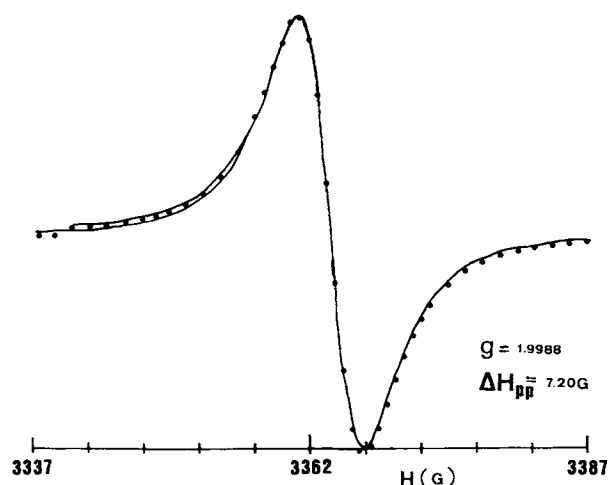
Figure 5 Comparison of ESR spectrum for powder PVK iodine-doped at 570 K (——) with theoretical spectrum (-•-•-).

iodine atmosphere at 470 K there is polymer degradation with NH_4I formation. ESR measurements as do σ measurements show that there are two kinds of samples:

- Those doped without any annealing.
- Those doped by annealing of the powder under iodine atmosphere, at $T = 370$ K or more.

The former are resistive, they have a great activation energy, and the ESR signal is small. The latter are more conductive, their activation energy is smaller, and the ESR signal increases by, at least, one order of magnitude.

We showed earlier[1,2] that there is polymer degradation when the annealing temperature is 470 or 570 K. This degradation is corroborated by Raman diffusion measurements (Fig. 2). The polymer degradation which began at 470 K is completed at 570 K under iodine pressure. We showed[2] that after degradation a new amorphous polymer appears with, embedded in its bulk, NH_4I crystallites. Therefore,

Scheme 2.

T 570K
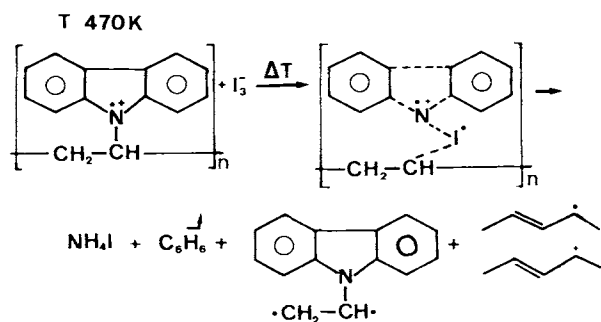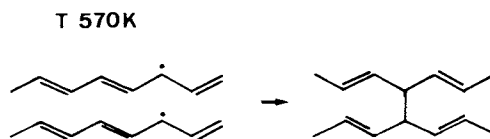
Scheme 3.

the two kinds of experimental comportment described above can be attributed to the samples before and after polymer degradation. The first class of samples consists of PVK powder doped with iodine at room temperature. The conductivity of these samples is about three orders of magnitude greater than that of pure PVK.[12] The conductivity increase corresponds to the ESR signal apparition. The origin of spins is a CT complex formation between PVK and iodine. The carriers so formed are localized on the carbazole units, since there are only π bonds in the aliphatic chains. Since $\sigma \propto \exp - [(E_a)/(kT)]$, we can imagine that the carrier's moving process is via hopping between localized states.[13] E_a is large, which can be attributed to a strong localization of the carriers. We showed earlier[1] that the chain lenghs decrease when the iodine-doped PVK is annealed at 370 K; however, the conductivities are the
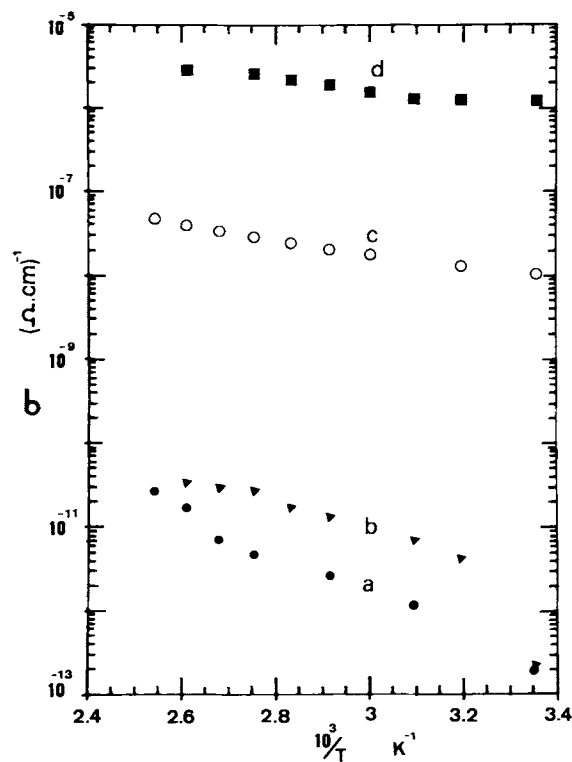

Figure 6 Conductivity of PVK powder doped with iodine: Ln σ vs. $1000/T$: (a) doping at room temperature; (b) doping at $T = 370$ K; (c) doping at $T = 470$ K; (d) doping at $T = 570$ K.
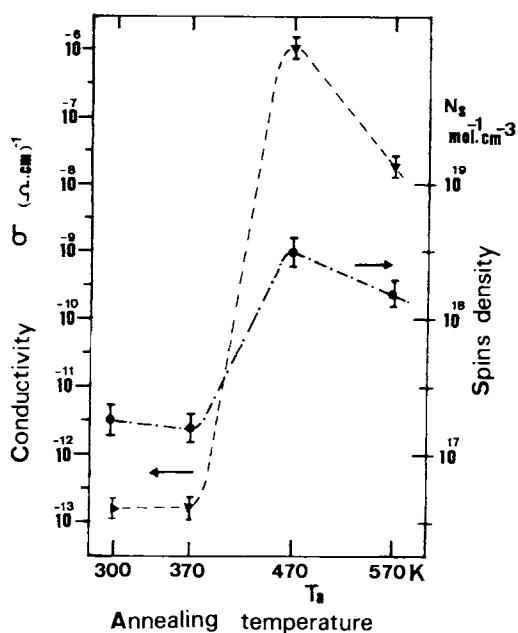
Figure 7 Evolution of the conductivity (σ) and of the spin density (N_S) with the annealing temperature (T_a) of PVK powder doped with iodine.

same (Table II) because the conductivity takes place only by hopping from one carbazole to another one, since there are no π bonds along the aliphatic chains.

At higher annealing temperature, the decrease of ΔH_{pp} corroborates the delocalization of spins. After polymer degradation, the ESR signal not only increases but also becomes isotropic. The former phenomenon corresponds to a carrier's density rise, and the latter, to carbon radical formation. This fact is in good accordance with the precipitation of NH_4I and the formation of a new amorphous polymer. The apparition of the carbon radical is probably related to the formation of $C=C$ bonds with π bonds in the new amorphous polymer (Scheme 3). Therefore, the carriers are free along the conjugated chain and the hopping process is needed only to jump from one conjugated chain to another one. The carriers are not as strongly localized as before; therefore, the activation energy E_a is smaller (Table II).

It can be seen in Figure 7 that the evolutions of the conductivity and of the spin density with the annealing temperature have the same shape, which shows the strong correlation between the conductivity and the carrier density. Moreover, Figure 8 shows us that there is a linear relation between the spin density N_S deduced from ESR measurements and the room-temperature conductivity (σ_{300K}). We can conclude that the increase of the conductivity is directly related to the increase of the carrier density.

Since $\sigma = e\mu N_S$, where e is the electronic charge; μ, the carrier's mobility; and N_S, the carrier's density, as N_S varies linearly with σ_{300K}, μ can be deduced from the slope of σ vs. N_S, which gives $\mu = 3 \cdot 10^{-7}$ cm^2 v^{-1} s^{-1}. This value is in good accordance with those obtained by other authors[14-18] by other methods (transient current, xerographic discharge).

The polymer degradation can only be roughly described. It can occur as described in Figure 5: Iodine, which is activated by heating, can attack the nitrogen of the carbazole units and then radicals will form along the chains. NH_4I formation will induce bond formation along the chains. Then, when the decomposition process is completed, there will be complete PVK degradation; all the carbazole units will react to form NH_4I and π bonds.

The carriers will move along the chains via π bonds and by hopping between the chains. Therefore, the evolution of the conductivity $\sigma \approx \exp - [(E_a)/(kT)]$ can be explained by the hopping process between the chains, the polymer being highly disordered. The activation energy is smaller than before because the carriers are not strongly localized on the chains. At higher temperature, the polymer will continue to be modified. There will be interactions between chain defects, which leads to a crosslinking reaction (Scheme 3). This interchain conformation will induce a decrease of the radical density, i.e., of the carrier density, and, therefore, there will be a decrease of the ESR signal and of the conductivity. This process can explain the strong increase of the ESR signal and of the conductivity after an annealing at 470 K and a slow decrease of both of them after the annealing at 570 K (Fig. 7).

CONCLUSION

The ESR and conductivity measurements are in good agreement with earlier studies[1,2] of iodine-doped PVK. When the PVK is doped at room temperature or at 370 K, there is only a decrease of the chain length with CT complex formation (between PVK and I) but there is no polymer degradation. The conductivity increase and the ESR signal apparition can be attributed to the CT complex. The conductivity can be attributed to carrier hopping between carbazole units. At higher annealing temperature, there is polymer degradation with NH_4I formation, i.e., there is graphitization of the polymer with π bond formation along the chains, which can explain the
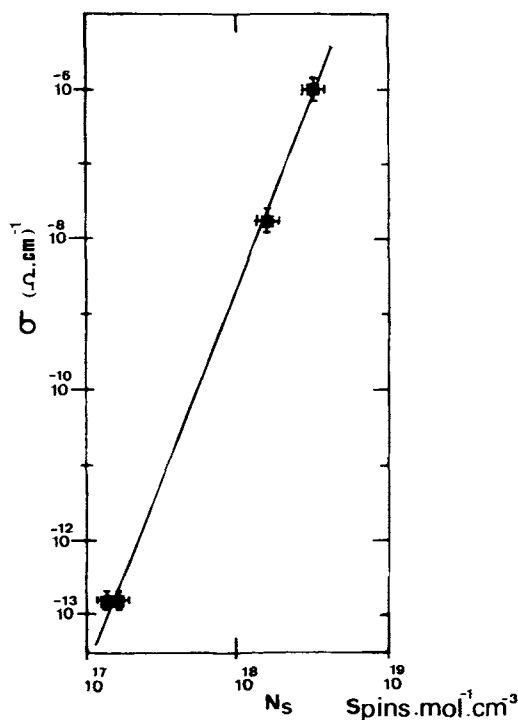
Figure 8   Evolution of σ vs. the spin density (N_S) when the annealing temperature of the doping of PVK powder with iodine varies.

strong increase of the conductivity. At higher temperature when the degradation process goes on, there is crosslinking between the chain with a decrease of the radical density, which can explain the small decrease of the conductivity and of the ESR signal.

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