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Inclusion of the cation iodonium (I_3^+) into the structure of poly(*N*-vinylcarbazole)

M.C. González[a], J.J. del Val[b], F. Zamora[a,*]

[a]*Dpto. Ciencia y Tecnología de Polímeros, Facultad de Química, Universidad del País Vasco, Apdo 1072, 20080 San Sebastian, Spain*
[b]*Dpto. Física de Materiales, Centro Mixto CSIC-UPV/EHU Facultad de Química, Universidad del País Vasco,*
Apdo 1072, 20080 San Sebastian, Spain

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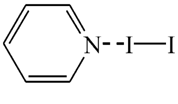
Abstract

Iodine is an usual doping agent used in order to improve the conductivity of insulator polymers with either aromatic and conjugated double bonds in their structure. This paper evidences the action of the cation iodonium on the conductivity of poly(*N*-vinylcarbazole) (PVK) and nitrosilated-PVK (PVK-NO). The cation is introduced via bis-pyridine-iodonium tetrafluoroborate salt ($IPYBF_4$) in both polymers yielding PVK–IPY-P and PVK-NO–IPY-P complexes, respectively, with a 1:1 ratio (carbazolyl/iodonium) in each. The complex extends the absorption band in the UV–Visible region and its IR spectrum shows characteristic bands. Both inter- and intra-molecular distances were modified in the polymer by the presence of iodonium as it is manifested by WAXS experiments. The thermal behaviour of the complex was studied by simultaneous thermogravimetry and differential thermal analysis being quite different from that of PVK. The polymer–IPY complex is stable till 200°C at which point the pyridine ligands loss takes place and results in a new structure of PVK-I^+ which is stable till 380°C and then is suddenly degraded. Elecrical conductivity of the complex improves with respect to that of PVK, but it does not overcome the semiconducting level achieved with other dopants.

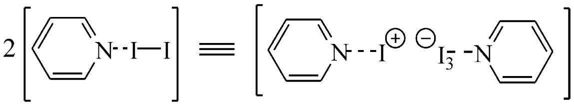
Keywords: Poly(*N*-vinylcarbazole); Iodonium salt; Polymer-complexes;

1. Introduction

The reaction of iodine with different aromatic solvents, e.g. pyridine, was studied by Kosower [1]. The posibility of iodine atoms being attached to the pyridinium ring by a covalent bond was seriously considered to yield the effective structure **(I)**. Later, the same author et al. [2] established that an intermolecular charge-transfer complex, in which the pyridinium ion acts as the electron-acceptor species, was formed **(II)**. Moreover, they found that this kind of complex does not necessarily belong with later redox processes.



(I)



(II)

A major difference between solid-phase structures and complexes in solution is in the fact that, although a given complex may have the same stoichiometry, e.g. 1:1, in both phases, while the complex will probably exist as discrete pairs containing single donor (D) and acceptor (A) molecules in solution, in the solid phase the structures usually consist of large stacks of alternate donor and acceptor molecules. In such cases the ratio aproaches to DAD and ADA better than AD. The 1:1 charge-transfer complex between iodine and pyridine should not be confused with the ionic compound, which has the stoichiometry 2 (I_2-pyridine). The structure of this latter compound has been determined by Hassel and Hope [3]. The distances between the halogen atoms, and the aromatic ring are within the range 3.23–3.38 Å, being a smaller value with respect to

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* Corresponding author.

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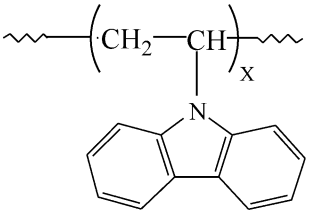
that of the van der Waals distance. The authors established that a structure like [pyridine-I^+–I_3^--pyridine] **(II)** must be assigned.

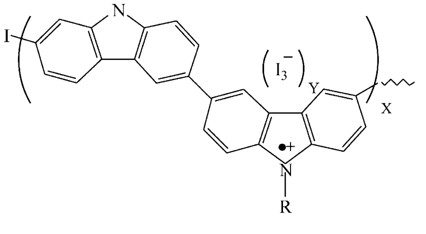
Poly(*N*-vinylcarbazole) (PVK) **(III)** is an efficient insulator in the darkness. However, it supports the passage of positive charge carriers, holes, which can be produced by exposure to UV-radiation or injected from certain types of electrodes towards a negatively charged electrode. Moreover, the generation of charge carriers can be shifted into the visible and near infrared range of wavelengths by proper sensitisers.



(III) *Repeat unit of the poly(N-vinylcarbazole)*

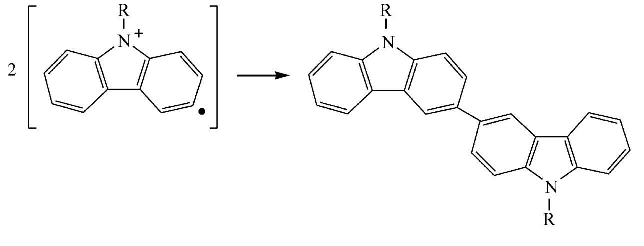
The additives, e.g. 2,4,7-trinitrofluorenone (TNF), which enhance photoconductivity properties of PVK are generally electron acceptors and may form donor–acceptor complexes, also called charge-transfer complexes (CTC), with carbazolyl units. External dyes have also been incorporated as dispersions in PVK for that purpose. Iodine, with an acceptor character, reacts against PVK to yield a poly(*N*-vinyl carbazole)–Iodine complex constituting a CTC [4,5].

The doping reaction is manifested between an oxidising or reducing reagent against a long-chain polyene, in terms of removal or addition of an electron. Iodine, I_2, is an oxidising agent or *p*-type dopant against poly(*N*-vinyl carbazole). From their mutual interaction, two molecules of iodine lead to both a negative iodine species, such as I_3^-, and a positive one, I^+, according to: $2I_2 = I^- + I_3^-$. These ions allow the simultaneous polymerisation and doping of highly conducting heterocyclic polycarbazole **(IV)** in liquid iodine [6,7]. The anion I_3^- is retained in the structure constituting a CTC and also showing plasticiser behaviour in poly(3,3′-*N*-alkylcarbazole) whose glass transition is centred at $T_g = 146°C$.



(IV) *Iodine-doped Complexes of Poly(3,3′-N-alkylcarbazolyl), with R=H, -CH$_3$*

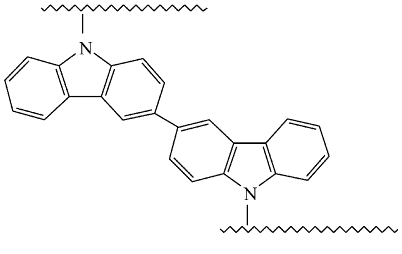
The electroinitiated polymerisation of 3-iodo-*N*-vinyl carbazole seems to be performed by a cationic mechanism [8]. In this process two samples were isolated: the soluble one corresponded to poly(3-iodo-*N*-vinyl carbazole) **(V)** and the other one to a polymer crosslinked by means of dicarbazolyl units **(VI)**. Ambrose and Nelson [9] have shown that carbazolyl and *N*-alkyl carbazolyl derivative dimerised when they were submitted to an electrochemical oxidation involving cation-radical species of a dark blue–green colour.



V

Partial oxidation of poly(*N*-vinyl carbazole) with *tri*-(*p*-bromophenyl) ammoniumyl hexachloroantimoniate(V) produces crosslinked PVK **(VI)** which contains dimeric carbazylium cation radicals and exhibits a significant semiconductivity [10], up to $10^{-5}\ \Omega^{-1}\ cm^{-1}$ at 20°C.

A structure based on an iodine–carbazole complex was produced by the presence of iodine cation-radical salts, which resulted from the transfer of an electron from dicarbazolyl moities to iodine, in the polycondensation of *trans*-1,2-bis(3-formyl-9-carbazolyl)cyclobutane with aromatic diamines [11]. The electrical conductivity of this iodine–polymer complex increases from 10^{-10} (undoped) to $10^{-5}\ \Omega^{-1}\ cm^{-1}$ (doped).



VI

As in the above cited materials the iodine is present as a neutral molecule in low molecular weight compounds (solvents) or as an anion, I_3^-, when a CTC was formed. The aim of this paper is to present a new polymeric structure based on poly(*N*-vinyl carbazole) incorporating the iodonium anion I^+.

The iodonium salts have been used in organic chemistry with differents purposes: (i) as an iodating agent, (ii) in order to achieve synthesis of regiospecific halo-olefines [12–14], (iii) as initiatiors of cationic polymerisation of *N*-vinylcarbazole by means of $Ar_2I^+X^-$ (with X: PF_6^-, SbF_6^-, AsF_5^-, etc.) by Ledwith and other authors [15,16]. Bipyridyl iodonium tetrafluoroborate (IPY) is a reactive of great versatile, able to take part in many different chemical processes and compatible with very diverse substances [12–14].

2. Experimental

Bipyridyl iodonium tetrafluoroborate (IPY) was kindly supplied by Dr Barluenga [12–14]. The IPY was recrystallised from dichloromethane solution from which yelow needle crystals were obtained. PVK was a commercial sample from BASF (Luvican®); the first fraction (PVK-FR1) of the polymer obtained by precipitation from a solvent/non-solvent (benzene/methanol) mixture was chosen for this study. The weight average molecular weight and the number average molecular weight were determined by gel permeation cromatography (GPC) being $\cong 4.2 \times 10^6$ and $\cong 1.8 \times 10^6$, respectively. A Waters gel permeation chromatograph with refraction index detector, tetrahydrofurane as eluent at 25°C and a microstiragel column set with pore size of 500, 10^4, 10^5, 10^6 Å was used. The columns were calibrated with monodisperse samples of polystyrene and the universal calibration method was applied by using the viscometric aquation for PVK in tetrahydrofurane at 25°C ($[\eta] = 1,44 \times 10^4\ \mathrm{M}^{0.65}$).

The experimental procedure to obtain the PVK–IPY complex was the following: PVK-FR1 (0.482 g) was dissolved in dichloromethane (100 ml, 0.025 M) and IPY (0.930 g) was also dissolved in this solvent (100 ml, 0.025 M). Both solutions were mixed at room temperature and after 15 min a precipitate of yellow–brown colour was detected. The reaction was accelerated if the mixture was heated at the refluxing temperature of the solvent. From the solution, a precipitate (PVK–IPY-P) was filtered, washed with dichloromethane (100 ml) and dried under reduced pressure (10^{-2} mmHg) for 24 h at 70°C. The remaining solution was added to methanol in excess and appeared a precipitated (PVK–IPY-S) which was filtered, washed and dried as earlier.

A nitrosation reaction was performed onto PVK solution (1%) in a solvent mixture dichloroethane/dimethylsulfoxide (50:30) by adding concentrared nitric acid (10 ml) at 60°C for 1 h. A yellowish-green solid (PVK-NO) was obtained resulting in nitrosilated carbazolyl units (95%). This polymer was submitted to reaction with IPY according to the procedure described above for PVK. The products were named as PVK-NO–IPY-P and PVK-NO–IPY-S, respectively.

Thermodegradative experiments were performed in a simultaneous thermal analyser, thermogravimetry (TG) and differential thermal analysis (DTA), from Polymer Laboratories (STA-1000). Around 10 mg of sample were heated from room temperature to 800°C at heating rate of 10°C min^{-1} under a nitrogen flow (10 ml min^{-1}).

The IR-spectra of the samples, in KBr pellets, were obtained in a Perkin–Elmer-FTIR 2000 using an interferometer resolution of 4 cm^{-1} and 25 spectra co-added.

A UV-Perkin–Elmer (Lambda 11) was used to obtain the UV-spectra of mixtures of PVK (0.025 M) and IPY (0.025 M) in dichloromethane, and also PVK-NO (0.025 M) and YPY (0.025 M) in dichloromethane, at different volume proportions (0:10; 4:6; 5:5; 6:4; 7:3; 8:2; and 10:0). The spectra were obtained just one minute after mixing the compounds. At longer times after the mixture a colloidal suspension appeared, that invalidated the quantitative results.

The wide angle X-ray scattering (WAXS) technique was applied in order to investigate the structural arrangement of the studied materials. Diffraction patterns were obtained at room temperature in a standard powder diffractometer composed of a Philips PW1729 X-ray generator and a vertical goniometer (Philips PW1820) provided with an automatic divergence slit and a graphite monochromator. CuKα radiation ($\lambda = 1.54$ Å) was used. Measurements were made by steps of 0.025° (2θ) with accumulation time of 5 s in an angular range between 0.3 and 3 $\mathrm{Å}^{-1}$ in scattering vector q values, defined as:

$$q = \frac{4\pi \sin\theta}{\lambda} \tag{1}$$

where 2θ is the scattering angle.

The electrical conductivity of both PVK–IPY-P and PVK-NO–IPY-P was measured at room temperature by direct contact between the mirror surfaces of stainless steel electrodes in a sandwich cell configuration using a Keithley (617) electrometer with a voltage source built-in. The flat pellet sample was obtained by compression moulding of powder in a proper die (20 mm diameter) under 10 tones pressure for 10 min.

3. Results and discussion

3.1. Chemical test

In order to check the presence of iodonium in the PVK complex, the following redox-test was performed in a biphasic system constituted of two immiscible solutions. The organic one composed by PVK–IPY-P (0.2 g), dry dichloromethane (20 ml) and tetrabutylaminetetrafluoroborate ($\mathrm{TBA^+BF_4^-}$) (0.086 g) and the aqueous solution containing the reducing agent $\mathrm{FeSO_4{\cdot}7H_2O}$ (10 ml, 0.04 M). After vigorous shaking of the mixture a pink colour, due to iodine, appeared in the organic phase giving a positive result.

After WAXS results it is explained that the result is a consequence of IPY molecules incorporated into the polymer in a manner similar to a crystalline stack. The iodonium ion remains in the polymer after the complex was heated at 200°C in air, however the above redox test was negative. The polymer complex remains insoluble

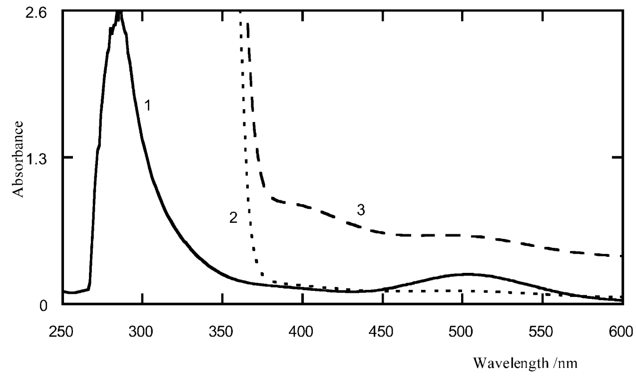


Fig. 1. UV spectra for: (1) IPY, (2) PVK and (3) PVK–IPY complex in solution.

indicating that a crosslinked structure was produced during the thermal treatment.

3.2. UV-spectroscopy

The pure IPY compound dissolved in dichloromethane shows an intense band centred at 286 nm and a small one at 503 nm. The PVK in dichloromethane showed an intense absorption due to the overlapped bands at 286–360 nm. Several distinct bands are noted for PVK in hexane around 345, 295, 260, 245, and 230 nm [17]. The UV spectrum of the complex PVK–IPY in dichloromethane is characterised by a new band placed at $\lambda = 400$ nm which overlaps with that of IPY at 500 nm, but not those at 345–350 nm of the PVK. Fig. 1 shows the spectra for the pure components and for the mixture (1:1) of both dissolved in dichloromethane.

The optical density of absorption at 400 nm, represented versus the molar fraction of PVK for each PVK–IPY solvent mixtures, established the maximum absorption for the ratio 0.88:1 (PVK/IPY). If we consider the structure of the complex formed as an iodonium-bipyridine molecule inserted between two carbazolyl units in a sandwich-like structure along the polymer chain, the complex composition should tend to a 1:1 limiting ratio. So the slight excess of IPY present induces to interpret that some molecules could be in a stacked structure, in the same way as it has been proposed for charge transfer complexes (CTC) among molecules with donor and acceptor character. This arrangement causes the crystallisation observed in WAXS experiments (see below).

3.3. FTIR-spectroscopy

The ocurrence of donor–acceptor interactions is usually accompanied by a decrease of some vibrational frequencies corresponding to one or both compounds. For example, the C=O band at 1745 cm^{-1} for trinitrofluorene (TNF) is shifted to 1735 cm^{-1} in the complex PVK–TNF [18]. Futhermore new specific peaks can appear as a result of the modification of both the dipole moment and the molecular symmetry indicating the formation of strong complexes.

Hermann and Rembaum [4] found the IR-spectra of both, the monomer (*N*-vinyl carbazole) and the PVK did not change after being complexed with iodine indicating that there was no significant reaction. However, the vinyl C–H deformation band at 1000 cm^{-1} is the main absorption band of undoped polyacetylene and, on exposure to any dopant (I_2 or AsF_5), two new strong bands appear at 1370 and 900 cm^{-1}. Some authors [19] attribute these bands to the delocalised charge carriers and the strength of the band is due to the coupling of these vibrations to the π-electrons. Greater exposure shows an increased absorption accross the whole infrared spectrum. This fact is common to polymers with conjugated structure as in the case of the IR spectrum of polypyrrol [20].

Fig. (2) shows the IR-spectra of IPY, PVK–IPY-P, PVK–IPY-S and PVK. The most significant differences between PVK and PVK–IPY-S are the peaks at 787 and 1271 cm^{-1} present in the PVK–IPY-S spectrum which are associated to the iodo-carbazolyl moiety in agreement to the spectrum of poly(3-iodo-*N*-vinylcarbazole) electrochemically polymerised [8].

In the PVK–IPY-P spectrum the band at 1529 cm^{-1} is associated to the carbazolyl–IPY complex. The small intensity of the peaks at 1271 and 787 cm^{-1} indicate that

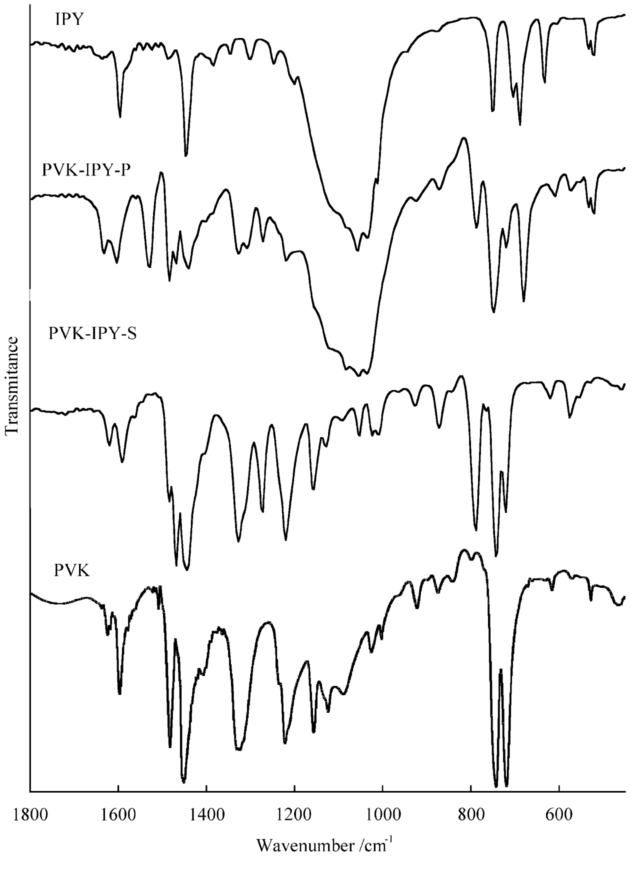


Fig. 2. IR spectra for: IPY, PVK–IPY-P, PVK–IPY-S and PVK.

a few iodo-carbazolyl is also present. After PVK–IPY-P sample was heated at 340°C and maintained for one hour in a nitrogen atmosphere, the spectrum of the residue was analogous to that of PVK–IPY-S. The band at 1529 cm^{-1} disappeared because the complex was decomposed at the same time than an additional halogenation reaction took place, and owing to this fact, the relative intensity of the bands 787 and 1271 cm^{-1} in the residue spectrum increased.

All IR characteristic bands of the IPY are also visible in PVK–IPY-P. The broad band between 990–1200 cm^{-1} is associated with the IPY molecules stacked in the solid and it disappeared after heating.

The modified PVK by nitrosation is a pale yellow–green solid which ressembles that described by K. Toluko [21]. Since the NO group in the carbazolyl unit increases the donor character, the PVK-NO–IPY-P complex was expected to be more stable. The complex bearing a brown–green colour shows a FTIR spectrum identical to that one for the complex formed with the unmodified polymer either for the precipitated portion or for the dissolved one. Table 1 shows the presence or not of the most characteristic IR bands for the whole of samples here studied.

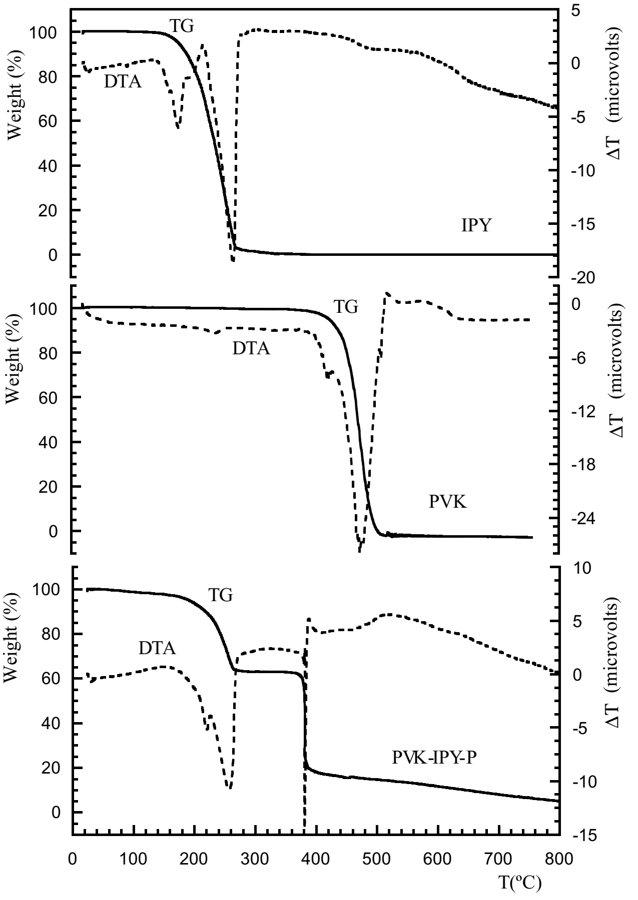


Fig. 3. TG and DTA curves for: IPY, PVK and PVK–IPY-P.

Table 1
Structural correlation distances corresponding to the glassy state of the polymer-complexes

Sample	Longer distance (Å)	Interchain distance (Å)	Intrachain distance (Å)
PVK	11.5	4.3	2.2
PVK–YPY-P		3.7	2.0
PVK(NO)	11.7	4.3	2.1
PVK(NO)–YPY-P		3.9	2.0

3.4. Thermogravimetry

Fig. 3 shows both TG and DTA curves for IPY, PVK and the complex PVK–IPY-P. The IPY sample gives a continuous loss of weight in the range 125–260°C yielding a residue of less than 5%. However, the simultaneous recorded DTA signal shows two well defined endotherms with maxima at 179 and 260°C and two shoulders at 162 and 200°C which indicate successive decomposition processes due to the loss of pyridine ligands below 200°C. Both, the maximum weight loss and the intense DTA endotherm around 250°C suggests that the major products of decomposition are volatilised and the residue (5%) could be a consequence of redox reactions during the volatilisation.

The thermogravimetric curve of PVK–IPY-P shows two steps. During the first one, the DTA signal shows the peaks asigned to IPY compound but shifted towards higher temperatures, probably because of a more stable sandwich-like structure between carbazolyl units. It is to be noted that the DTA interval temperature is at the same interval that the PVK glass transition is manifested. So, the local motions of chain segments favour the stacked units to move away and it would correspond with the 10–12% of weight loss in the first degradation step. According to the TG curve of IPY the pyridine ligands molecules could also be detached in this step.

DTA signal and product weight just remain stable between 260 and 390°C and the chemical test performed on product sample from this step produced a negative result, however iodonium cations are in the polymer, as it could be deduced from WAXS experiments (see below), and degradation of PVK is strongly affected by these cations. A second abrupt degradation step involving a weight loss around 37% and a sharp endotherm in the DTA signal at 379°C are associated with a redox reaction producing a carbocation in PVK that provokes a rapid scission of the polymer chain which can yield, in part, iodocarbazolyl derivatives able to develop grafitic reactions at temperatures over 500°C. This is a well documented reaction in which diaryliodonium salts act as nucleophiles giving haloderivatives by heating. This behaviour is not shown in PVK degradation, however, the rapid evolution ressembles that shown by dinitrated PVK at high temperatures in which carbocationic species formed between the carbazolyl and nitrated carbazolyl units constituted CTC units [22,23].

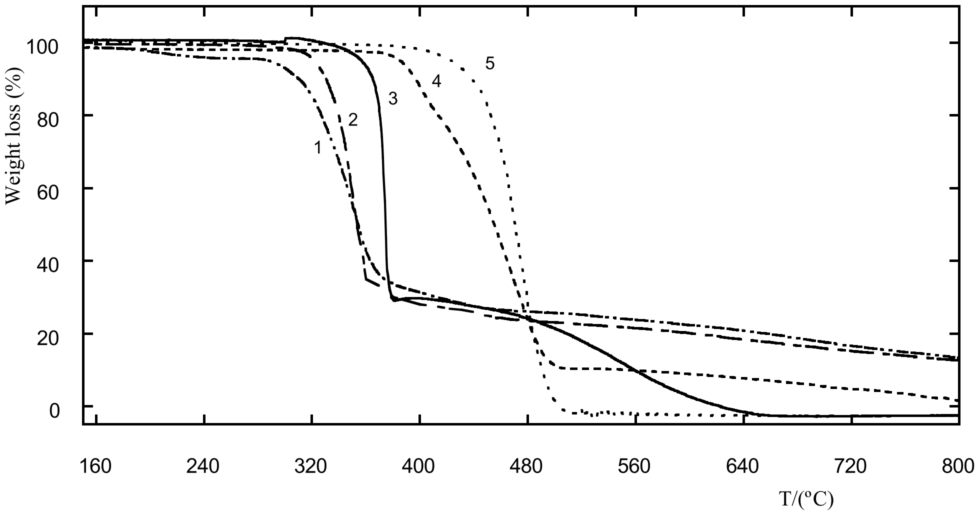


Fig. 4. Thermogravimetric curves for: (1) PVK-NO–IPY-S, (2) PVK–IPY-S, (3) PVK–I^+ (complex), (4) PVK-NO, and (5) PVK samples.

By comparing the thermogram of PVK–IPY-P (Fig. 3) with that of PVK–IPY-S (Fig. 4) it is clear that the latter manifests only one degradation step and it could be accepted that IPY is not present as a complex there. Its IR spectrum puts in evidence the presence of the halogen derivative which modifies the aromatic vibration bands, so we can conclude that the soluble compound PVK–IPY-S corresponds to modified heterogeneous halogenated PVK.

Fig. 4 shows the TG curves of PVK, PVK-NO, PVK–IPY-S, PVK-NO–IPY-S and PVK–I^+ (complex). These thermograms distinguish the different withdrawing electron effect of both NO and iodide groups attached to carbazolyl units. As expected, the starting degradation temperature is lower as the withdrawing action increases at the same time it yields higher percentage of residue (about 15%) indicating a preferential scission of the chemical carbazolyl modified units against unmodified ones.

The thermal degradation of PVK-NO–IPY-P shows very small differences with respect to that of the PVP–IPY-P which must be attributed to the presence of the NO groups.

When PVK–IPY-P was heated to 300°C, held for 1 h, and cooled down to room temperature (PVK–I^+), the next run to 800°C gave a thermogram which manifests only one weight loss step of about 80% at the same temperature interval as the second degradation step of the PVK–IPY-P. The IR spectrum of the sample PVK–I^+ coincides with that of PVK–IPY-S, but their thermodegradation processes are different, as it can be seen in Fig. (4). This behaviour confirms that iodonium cations remain in the PVK at 380–390°C without pyridine. The residue at 400°C is considerably higher (30%) than that presented by the PVK–IPY-P without this thermal treatment and its subsequent evolution results in a well defined exothermic process by DTA probably due to a graphitic structure arising from the iodocarbazole degraded units.

3.5. Wide angle X-ray scattering (WAXS)

The WAXS patterns (see Fig. 5) were obtained at room temperature for pure PVK, PVK–IPY-P, PVK(NO)–IPY-P and PVK–I^+ (complex) after heating to 300°C (first plateau).

Two main diffraction peaks (it can be observed as an intermediate shoulder between them) are detected in pure PVK at 0.5 and 1.49 $Å^{-1}$, corresponding to characteristic structural correlation distances of 11.5 and 4.3 Å, respectively. The longest distance corresponds very well to the interchain packing in crystalline PVK, reported as being between 10.8 and 12 Å [17]. In this case, PVK is amorphous, and the first diffraction peak can be seen as constituting a nucleus of some interchain ordering that can give rise to a crystalline order after annealing at temperatures higher than T_g, as noted elsewhere [24]. The second peak reflects shorter structural correlation distances, which could originate from interchain correlations within side-chain carbazolyl groups [25,26]. A third lower peak at around 2.86 $Å^{-1}$ corresponds to intrachain correlations distances that are on average 2.2 Å.

PVK–IPY-P and PVK-NO–IPY-P samples show a clear semicrystalline character with some sharp peaks (corresponding to interatomic spacings of 4.3, 3.7 and 2.8 Å in the two samples) overlapped on the background produced by the amorphous phase. The amount of crystallinity χ can be evaluated at first approximation by:

$$\chi = \frac{\int_0^\infty q^2 I_c \, dq}{\int_0^\infty q^2 I \, dq} \qquad (2)$$

where I_c denotes the intensity corresponding to the crystalline peaks, that is the experimental intensity substracted from the intensity corresponding the amorphous background [27]. Low χ values (between 2 and 3%) were

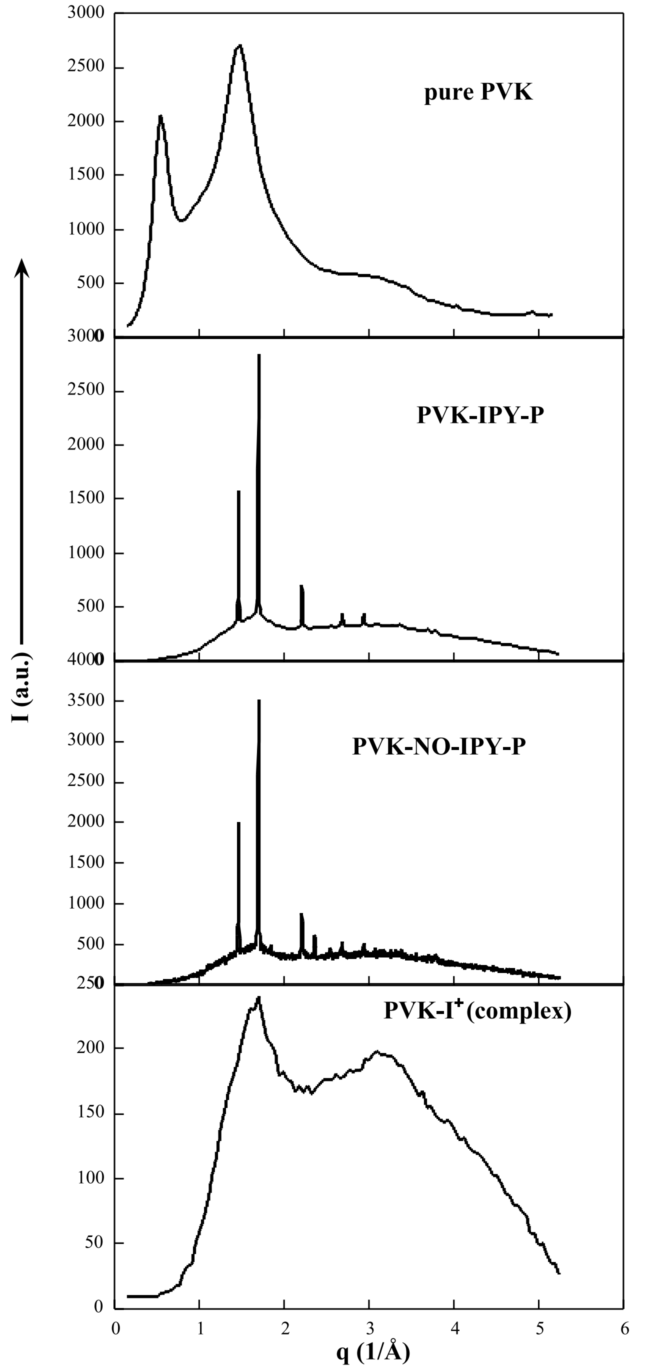


Fig. 5. WAXS pattern for: PVK, PVK–IPY-P, PVK-NO–IPY-P and PVK–I^+ (complex) samples.

obtained for the two samples. These crystallinity amounts must be associated to the stack structure of IPY molecules when they complex with carbazolyl units. These crystalline peaks are superimposed on to a typical WAXS curve proper of glassy materials (as are pure PVK and PVK-NO) with large diffraction maxima that correspond to interchain structural correlations. After the introduction of IPY units into the polymer structure, the diffraction corresponding to the amorphous regions shows that the first diffraction halo has been disappeared and the second one corresponding to interchain correlations is shifted towards shorter interchain distances, and hence, correlated to side-chain carbazolyl groups. This fact can be explained in the way that two carbazolyl groups acting as sandwich leaves (face to face) need to open some angle to accommodate the IPY but at the same time the helical structure of the PVK becomes more extended and rigid. The distances between a leaf of the sandwich and other adjacent carbazolyl ones -not involved in the complexation- decrease. In the WAXS patterns, this change leads to a shifting of the peak at 1.48 $Å^{-1}$ in PVK to 1.68 $Å^{-1}$ in PVK–IPY-P sample which means that the interchain distances characteristic of PVK are decreased (see Table 1). The same effect is produced with the intrachain correlations. In this case, the higher relative intensity (in comparison to the main interchain peak) obtained or the high q peak (shorter correlation distances) indicates that the number of these intrachain correlations has been increased with the introduction of the YPY units in the pure polymer.

The results are similar in the case of PVK-NO–IPY-P notifying different values of such distances motivated by the different electronegativity of the carbazolyl units supporting the nitrosyl groups. These significant correlation distances are listed in Table 1.

3.6. Electrical conductivity measurements

The electrical resistivity of PVK is in the range 10^{12}–10^{16} Ω m over the temperature range 25–150°C. In most cases, in this and in other insulating polymers, hole migration is the dominant mechanism, although, with iodine as dopant, electron mobility is also present. However, some authors make the claim for a hopping mechanism between traps [17]. The electrical conductivity properties of CTC have been reviewed by Simionescu and Grigoras [28] and a significant increase of the electrical conductivity has been noticed in the case of a sandwich-like structure of active groups with respect to the small molecular complexes. This fact can be due to the closer packing which implies superposition of the p-orbitals including an intensification of the CTC interactions and, so, an increase of carrier mobility. In this way the increase of crystallinity in the complex is positively reflected in the mobility of carriers, and so, in the conductivity of the sample. Consequently, charge carriers have an electronic nature and not an ionic character.

Resistivity values of PVK–IPY-P and PVK(NO)–IPY-P change with E (electric field strength) in a non linear ratio indicating a semiconductor material. Plots of the current density, J, and log J versus $E^{1/2}$ are linear for E values higher than 40 000 V m^{-1}. So, the conductor mechanism could not be distinguished if it was determined by Schotkky or/and by Poole–Frenkel effects. Fig. (6) shows the resistivity, ρ, against the applied field E, for the above samples. The resistivity of both decreases as the field increases going through a minimum from which some internal overfield opposes to the current passage and subsequent resistivity

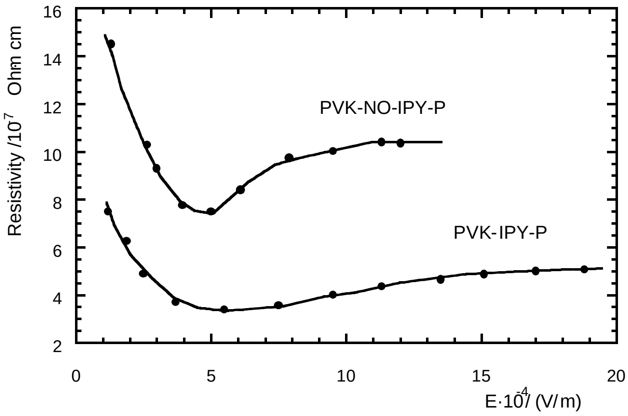


Fig. 6. Resistivity versus electric field for PVK–IPY-P and PVK-NO-IPY-P samples.

increases. This is probably a consequence of the spatial current limiting effect and in consequence the mechanism of conduction would be developed by hopping between traps. As the PVK(NO) develops a more intense interaction with iodonium cation, the conductivity of the sample results less than that of the PVK–IPY because the carbazolyl–iodonium–carbazolyl complex could delay the mobility of carriers acting more efficiently as a traping system.

The cristallinity (2–3%) of the stacked IPY molecules in the polymer affects either the resistivity values as in the mechanism as well. When the PVK–IPY-P is heated, at 200°C, in air atmosphere, both iodonium and pyridine molecules are lost, giving resistivity values such as $\rho = -0.3 \times 10^{11}\ \Omega$ m for $E = 1.82 \times 10^4$ V m^{-1} and $\rho = -12.7 \times 10^{11}\ \Omega$ m for $E = 18.18 \times 10^4$ V m^{-1}) confirming that this decrease is by the sandwich structure developed between iodonium and carbazolyl leaves. In this case the sign of the current changed to negative because the current changes from an electronic character to a holes mechanism. In Table 2 are conductivity values for samples of this work and those for similar samples referenced in the bibliography.

4. Conclusions

A polymeric complex structure between IPY and PVK has been obtained, characterised by specific IR bands, and its structure interpreted by means of WAXS analysis notifying a crystalline stack of IPY molecules in the PVK–IPY complex which modifyies the amorphous state of the polymer. The complex initially formed changes to a more stable structure (PVK–I$^+$) ($^-$BF$_4$). A tentative mechanism to interpret its behaviour with the temperature is shown below:

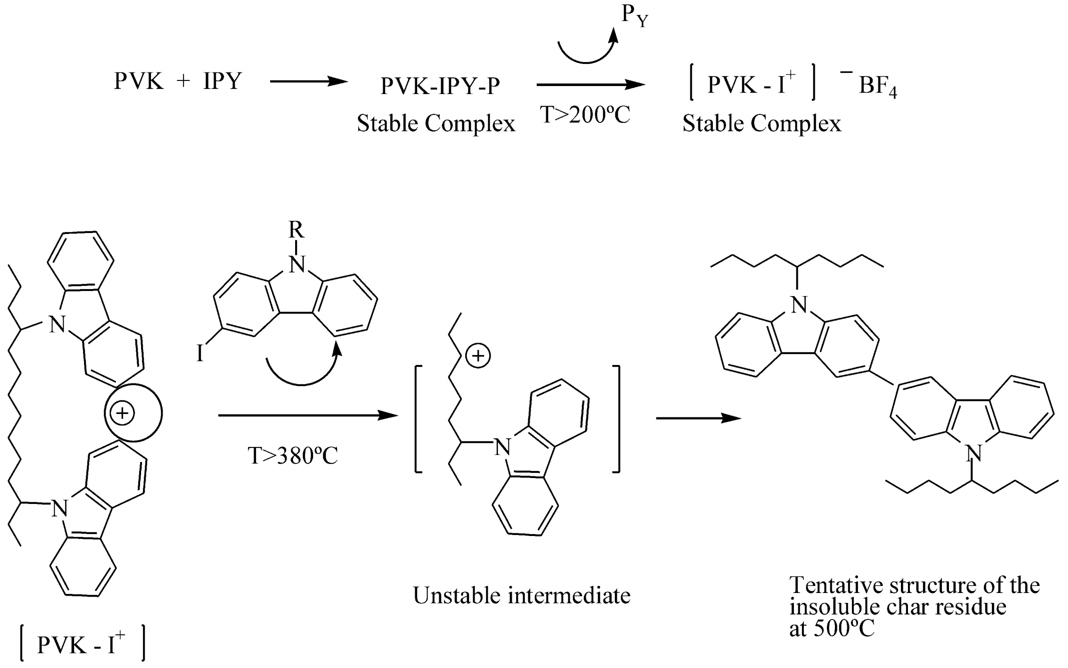


Table 2

Conductivity values for PVK, some related carbazolyl-containing polymers doped with iodine and complex systems formed with PVK–IPY (maximum value), PVK(NO)–IPY (maximum value)

Sample	Conductivity (Ω^{-1} cm^{-1})	Reference
PVK	10^{-14}	[17]
PVK–I$_2$ (77%)	10^{-5}	[4,5]
Cation/radical-PVK	10^{-5}–10^{-13}	[10]
Carbazole-containing polymer (I$_2$-doped)	10^{-3}	[11]
Poly(carbazole) (I$_2$-doped)	1–10	[6,7]
PVK–IPY	3×10^{-6}	This work
PVK(NO)–IPY	1×10^{-6}	This work
PVK–IPY (after 200°C)	12.7×10^{-9}	This work

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