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D.c.-conductivity of poly(*N*-vinylcarbazole) containing iron(III)-phthalocyanine side-units

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Iron(III)-phthalocyanine has been grafted onto poly(*N*-vinylcarbazole) to change the dielectric character of the polymer and improve electrical conductivity. Either unfractionated or fractionated polymer samples were submitted to grafting reactions. From a chemical point of view the grafted samples differ from each other in terms of the eventual chemical group joining the phthalocyanine unit to a carbazyl group, the content of unreacted amino groups, and the inter- or intramolecular charge-transfer-complex units formed between the donor (amino-carbazyl derived) and the acceptor (nitro-carbazyl derived) moieties. Molecular weight differences of the polymer samples produce little variation in conductivity of the grafted samples, whereas the above chemical aspects, heating rate and temperature influence the conductor mechanism. The density data currently obtained fit the Richardson–Schottky equation for dielectric materials well. The trapping parameter was calculated by applying Child's law. The activation energy values obtained can be explained attending to conformational changes that, in any sample, will be able to favour conductivity at high temperatures, between 180 and 200°C, whereas conductive electrical motions are related to the formation of charge-transfer-complexes near room temperature. Copyright © 1996 Elsevier Science Ltd.

(Keywords: phthalocyanines; poly(*N*-vinylcarbazole); d.c.-conductivity)

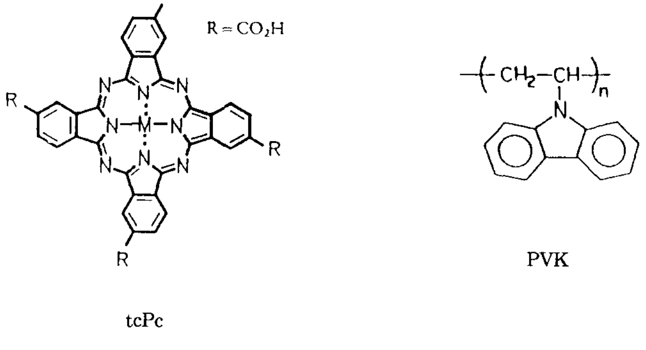
INTRODUCTION

Research on metal-containing polymers began three decades ago with the discovery of polymers incorporating a potential reactive metal-ion. These polymers have a wide range of applications, such as semiconductors[1], catalysts[2] or controlled release agents for drugs and biocides[3].

Most practical polymers based on electrographic photoreceptor systems now in use are in fact solid solutions of active species in a binder host polymer[4]. This system embodies the notion of full chemical control on the charge transport process. Thus the concentration of dopant molecules directly controls the drift mobility, which is in turn controlled by wavefunction overlap between active sites. It is now recognized that charge transport in amorphous sigma-bonded carbon backbone polymers undergoes a hopping process which involves local electric field driven charge exchanges among discrete sites which are dissolved molecules or covalently bonded functional pendant groups[5].

Inherent to semiconductor materials, as is the case with poly(*N*-vinylcarbazole) (PVK), is the existence of charge-carrier traps which provoke sensible variations in the steady-state conduction, limiting the conduction process markedly, and so also the freedom of charge-carrier motion. It would be of interest to quantify both the number and the energy of the traps, in order to distinguish between different dielectric materials.

The present contribution deals with chemical modifications of a well known photoconductor polymer, PVK[6], with 2,9,16,23-tetracarboxy-iron(III)-phthalocyanine (tcPc) (see *Scheme 1*) which belongs to a class of compounds largely utilized as pigment agents. Taking into account the availability of the polymer to be modified through its carbazyl pendant groups, and the paramagnetic properties of tcPc[7], new organometal containing polymers, with a certain degree of conductivity and easier processing, can be obtained. Moreover, it seems obvious that grafting reactions of such a bulky moiety as tcPc can provoke conformational changes in



Scheme 1

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the polymer, and so certain modifications of its physical properties will occur (i.e. chain flexibility, glass transition temperature, thermal stability and even conductivity). The chemical procedures applied have been tailored in order for the resulting grafted compounds to present a ceto (–CO–) or amido (–HNCO–) group in the junction between a tcPc unit and a carbazyl group.

A metal–insulator interface is a limiting factor of the conductor process in semiconductor materials, and that is taken into account in Schottky's effect, which gives valuable energetic information about apparent trap depth, according to the nature of the dielectric material[8]. The Richardson–Schottky equation is given by:

$$J = AT^2 \exp(-W/kT) \exp(\Delta W_s/kT) \qquad (1)$$

where J is the steady-state current density crossing over the metal–insulator interface, A is Richardson's constant, k is Boltzmann's constant, W is the electrode work function, T is the temperature, and ΔW_s is the decrease of the potential barrier which depends on the applied electric field, E, as follows:

$$\Delta W_s = \frac{e^{3/2}}{2\pi^{1/2}\epsilon^{1/2}} E^{1/2} = \beta_s E^{1/2} \qquad (2)$$

ϵ being the dielectric constant, e the electron charge, and β_s the proportional constant.

If potential barriers to the charge injection are assumed, J is not a function of position and is related to the applied potential, V, by Child's law[8] for a trap-free insulator as follows:

$$J = \frac{9\epsilon\mu V^2}{8d^3} \qquad (3)$$

μ being the mobility of the carriers and d the distance between electrodes (or sample thickness). The existence of discrete arrays of traps in a conductor solid make the space–charge-limited current decrease, and equation (3) is modified by a trap-limiting parameter, θ, which states the ratio of trapped charge to free charge. Finally, the estimate of activation energies gives us useful information about a likely conductor mechanism.

EXPERIMENTAL

Three samples of PVK (Luvican®-BASF), labelled A, B and C in *Table 1*, were fractionated separately by a conventional method at 25°C using benzene–methanol as the solvent–non solvent system. Molecular weights were determined by viscometry in tetrahydrofuran at 25°C, and gel permeation chromatography (g.p.c.) in tetrahydrofuran at 25°C by using the Mark–Houwink–Sakurada (MHS) constants[9] ($K = 1.44 \times 10^{-7}\,\mathrm{m^3\,kg^{-1}}$ and $a = 0.65$). TcPc was synthesized from trimellitic acid following a referenced method[10].

Sample A and four of its homodispersed fractions were submitted one by one to mononitration reactions[11], reduction of nitro groups to corresponding amino-derived groups, and then reacted with tcPc in dimethylsulfoxide medium. Products are numbered A in *Table 1*. Likewise, sample B and four of its fractions were selected to be dinitrated[12], reduced to diamino-derived form, and then reacted with tcPc in dimethylsulfoxide medium. They are numbered B in *Table 1*. Finally, sample C and five of its fractions were reacted with tcPc–halide under Friedel–Crafts condictions, following the procedure described by Shirai *et al.*[10]. These products are numbered C in *Table 1*.

In order to find out grafting percentages, a little portion of each grafted sample was digested in heat with a sulfuric–nitric acid mixture (1/1 v/v), to obtain the corresponding ferric salt. Quantitative determinations of Fe(III) were attempted by the well known phenantroline spectroscopic method, at 508 nm.

To carry out the conductivity of the samples, disc-shaped compressed pellets of 20 mm diameter and around 0.3 mm thickness were made by pressing 10 tons for 20 min in a vacuum. A pellet was placed in a conductivity cell of parallel stainless-steel electrodes and provided with a guarded ring. Electrical variables were controlled using an electrometer (Keithley mod. 617 with a voltage source built in) linked up to the cell conductivity. Temperature was controlled by means of a thermocouple inside the cell and connected to a temperature programmer (West mod. 2050 PID).

A set of a thermocouple inside the cell and connected to a temperature programmer (West mod. 2050 PID).

Table 1 Molecular weight, M_w, and polydispersity index, PI, of PVK samples before grafting. Electrical parameters, β and θ, obtained from electrical data at 30°C for tcPc grafted PVK-fractions

Sample	$M_w \times 10^{-6}$	PI	Percentage of grafted tcPc	β ($10^{-23}\,\mathrm{J\,m^{1/2}V^{-1/2}}$)	θ
A-1	0.38	1.5	0.12	3.01	0.26
A-2	0.26	1.3	6.54	1.76	0.14
A-3	0.10	1.2	1.07	1.71	0.09
A-4	0.06	1.3	0.33	1.51	0.05
A	0.50	8.1	0.35		
B-1	2.65	2.2	<0.01	3.18	0.13
B-2	1.67	1.7	<0.01	3.68	0.31
B-3	0.93	1.5	<0.01	4.18	0.44
B-4	0.42	1.4	<0.01	4.39	0.47
B	1.74	4.7	<0.01		
C-1	5.80	1.8	1.07	3.21	0.14
C-2	4.85	1.8	1.80	3.29	0.25
C-3	3.26	1.5	1.48	3.27	0.26
C-4	1.19	1.6	2.68	3.20	0.30
C-5	0.71	1.5	0.87	3.26	0.25
C	2.67	5.6	0.62		

A set of electrical experiments applied to each grafted PVK-fraction consisted of measuring steady-state current densities after bias 20, 40, 60, 80 and 100 V, respectively, at 30°C. Before applying a new voltage value, samples were subjected to 100 V for 30 min and subsequently released for 2 h, in order to delete the electrical history previously acquired.

In addition, a set of both dynamic and isothermal thermoelectric experiments were only applied to grafted PVK-unfractionated samples (A, B and C) as follows. The dynamic experiments consisted of applying 80 V and keeping this constant while the temperature was varied from 30 to 200°C at heating rates of 2, 4, 6, 8 and 10°C min^{-1} in successive runs. Each time the sample reached 200°C the voltage was turned off, but temperature kept at 200°C for 30 min, in order the sample erased the previous electrical history acquired. The isothermal experiments consisted of applying 100 V at a fixed constant temperature and recording the resulting steady-state current density value. The chosen temperatures were 30, 35, 40, 45 and 50°C, which will be referred to as the low temperature interval in the next section; and temperatures of 180, 185, 190, 195 and 200°C which will be referred to as the high temperature interval.

RESULTS AND DISCUSSION

In *Table 1* are listed average weight-molecular weights (M_w) and polydispersity index (PI) of PVK samples submitted to grafting reactions. Grafting degrees are given by the percentage of tcPc grafted (also listed in *Table 1*). The proportion of tcPc grafted in the B samples was below the detection limit of iron by the phenanthroline method, although e.p.r. (electron paramagnetic resonance) spectra evidenced the presence of Fe(III) atoms[13,14], which reveals the effectiveness of grafting reactions, but in a minor yield. Dinitro-PVK should offer a better capability for grafting due to its availabilty to form amide groups, but as the reaction from nitro to amino-derived progresses charge transfer complex units (CTC) began to form and probably hindered grafting of tcPc units to the polymer.

To evaluate both the molecular weight and the grafting degree influence on charge conduction of grafted PVK fractions, electrical data from the above-mentioned measurements at 30°C was used in the Richardson-Schottky equation to calculate β and θ parameters, which give us knowledge about energy and the number of traps, respectively. Introduction of equation (2) into equation (1) leads to:

$$J = A' \exp(\beta E^{1/2}/kT) \qquad (4)$$

A' being a constant temperature dependent, and β an intrinsic parameter whose value can be determined by the chemical structure of the dielectric material, and factors such as distances among conducting units, electrostatic forces, or charge mobilities.

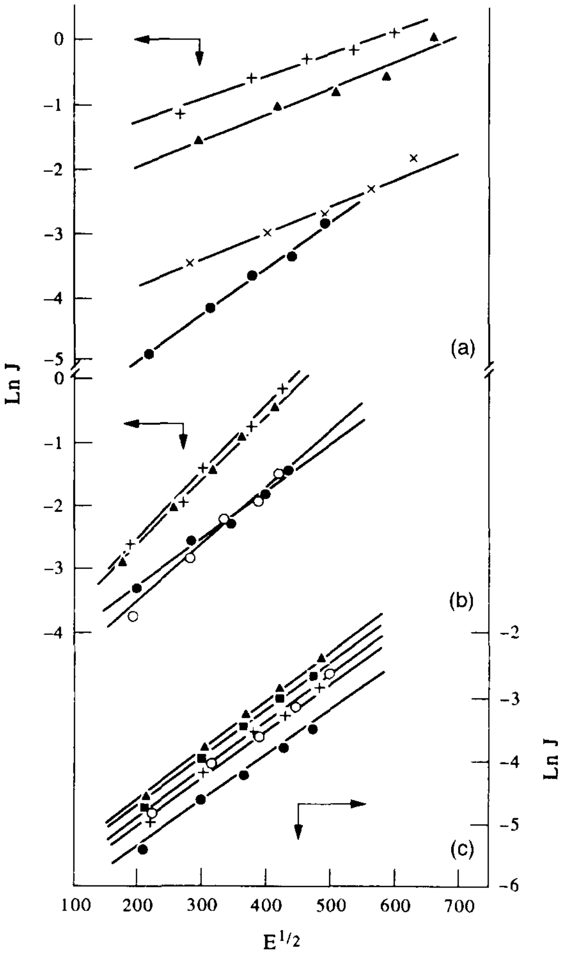

Figure 1 Plots of ln J vs $E^{1/2}$ for samples (a): ●, A-1; ×, A-2; ▲, A-3; +, A-4; (b): ●, B-1; ○, B-2; ▲, B-3; +, B-4; (c): ●, C-1; ■, C-2; ▲, C-3; +, C-4; ○, C-5

The plot of ln J vs $E^{1/2}$ for grafted C fractions (*Figure 1*) shows parallel straight lines, and β values were calculated from the gradients. It is not possible to establish any dependence between molecular weight and grafting percentage since closed β values resulted. The same plot for grafted A fractions in *Figure 1* shows higher J values as molecular weight decreases, irrespective of the tcPc content, i.e. the sample A-2 has a tcPc content over fifty times higher than the other A-samples, but it gives minor J values; meanwhile the sample with the highest molecular weight, A-1, exhibits both slope and J values of the same order of magnitude as the C samples, in spite of it having a tcPc content very much lower than those of the C samples. The above might be due to either A-1 or C fractions having a molecular weight inside the molecular weight range in which the PVK acquires a random coil conformation[15], whose chain disorder is able to promote larger distances between conductive units (tcPc), and this could favour the appearance of trap centres. The high current density values manifested by samples A-2, A-3 and A-4 could be attributed, on the one hand, to the remaining unreacted amino groups (acting as donors of charge carriers), since only a few of them were involved in the grafting. On the other hand, their lower molecular weights, near to a rod-like conformation, permit charge carriers to move primarily along the chain from a tcPc-carbazyl array to an adjacent one in the same polymer chain, just as in the case of anthracene where carriers move from one anthracene molecule to one adjacent in the molecular lattice[16]. According to the above, B samples should present higher J values because they come from the amination of dinitro-PVK but, due to generated CTCs, few amino groups are free to improve conductivity. The plot of ln J vs $E^{1/2}$ for B fractions in *Figure 1* also showed closed straight lines with little dependence on molecular weight, but J takes values of a higher order of magnitude than those for the C samples. In *Table 1* are listed β values and it can be seen that the highest steady-state current density values, and so minor β values, are exhibited by those grafting samples coming from monoamino low molecular weight PVK-fractions for reasons explained above.

In order to obtain the proportion of trapped charge carriers, plots of J vs V^2 according to equation (3) were attempted. Changes in the gradients indicated the presence of trap states. The trapping parameter (θ) for each sample was calculated from the ratio of the gradients after and before the break, and values are listed in *Table 1*. The θ values obtained have no correlation with grafting percentage, but molecular weight dependence is different for the three kinds of samples; i.e. as molecular weight is minor, θ values decrease for A fractions and increase for the B fractions, but follow a random variation against molecular weight for the C fractions. By comparing β and θ values, given in *Table 1*, it is appreciated that θ decreases as β does and vice versa, i.e. a minor trapped charge corresponds to a minor β value, so that charge carriers must overcome a lower energy barrier, as in agreement with equation (2).

Taking into account the different chemical structure of tcPc grafted-PVK samples, and since molecular weight has no correlation with the grafting percentage, the values of both θ and β parameters could be explained in the following manner. A samples have tcPc units joined to carbazyl ones through amido groups (–HNCO–) and also a great proportion of unreacted amino groups (–NH_2), favouring conductivity, so that low θ values result. B samples, although having discrete tcPc units grafted, are nevertheless basically composed of CTC units, which are able to act as trap centres for charge carriers, so that high θ values result. Finally, C samples, having a higher proportion of tcPc units, favour interactions between cofacially stacked tcPc units randomly disposed in the bulk[17], which would act as trapping centres.

To evaluate temperature effects on the bulk d.c.-conductivity (σ) thermoelectrical experiments were performed on A, B and C as described in Experimental. From the electrical data of dynamic thermoelectrical experiments, $\ln \sigma$ vs $1/T$, at 2, 4, 6, 8 and 10°C min^{-1} heating rates were plotted for the three samples, all of them showing curve lines which do not fit the Arrhenius mechanism, throughout the temperature interval applied. For instance, in *Figure 2* is shown the behaviour of sample B, in which curves are shifted to higher conductivity values as the heating rate increases. In this sense, high heating rates are required to achieve a major conductivity. The most significant result is an abrupt conductivity change when temperature is scanned from low to high values, showing higher conductivity values at low temperatures. It could be associated with short range conformational changes as a consequence of both heat and electric field effects on the conductive units[18]. Since the main glass transition was not detected in any of the samples by differential scanning calorimetry (d.s.c.) in the temperature interval studied, it is assumed that no long range motions were involved. Rather, such changes are interpreted as a disruption of conducting units, which provokes the separation of those cofacially disposed phthalocyanine units[17] in the case of samples A and C, with a partial disruption of CTC units in the B sample. Disruption motions are responsible for low conductivity.

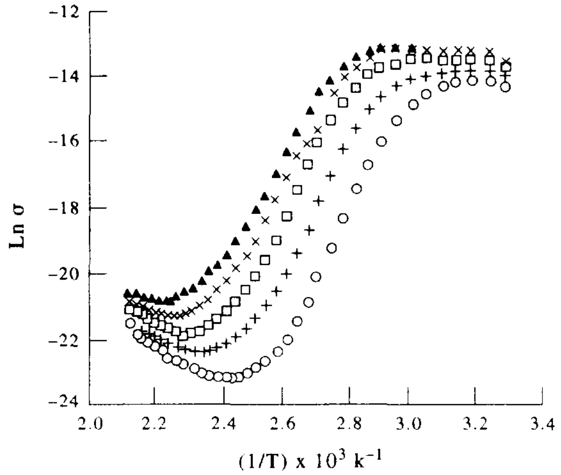

Figure 2 Plots of $\ln \sigma$ vs $1/T$ at heating rates of: ○, 2; +, 4; □, 6; ×, 8; and ▲, 10°C min^{-1} for sample B

Figure 3 is a comparative plot of $\ln \sigma$ vs $1/T$ of experiments performed at 6°C min^{-1} heating rate on A, B and C. The three curves show the above abrupt change and differ in the σ values obtained, both at low (before

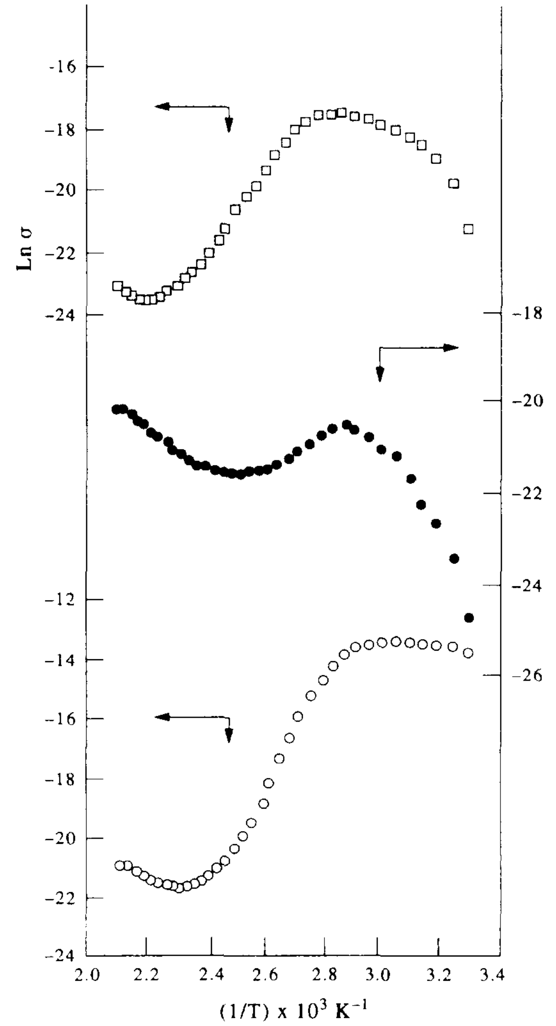

Figure 3 Plots of $\ln \sigma$ vs $1/T$ at 6°C min^{-1} heating rate for samples: □, A; ○, B; and ●, C

conformational change) and at high temperature intervals (after conformational change). Sample B seems to be the most conductive at the low temperature interval, so being the CTC units as the main contributors to conductivity, since CTCs structure favours the electrical charge dislocation. However, at high temperatures, short range movements cause the conducting units to be placed too far from each other, and conductivity decreases. Sample A is more flexible due to the amido linking groups, in that conductive units are more distant, and so conductivity is minor at high temperatures. Sample C presents the lowest conductivity at low temperatures since it has no amino groups, and furthermore its ceto linking groups are rigid enough, and avoid a suitable overlap of active sites for charge carriers to move easily. However at high temperatures the order of magnitude of σ values increases from 10^{-11} up to 10^{-9} A cm^{-2} yielding the major conductivity of the samples. Thus, thermal activation affected the three kinds of samples differently, when the same and constant electric field was applied.

The general power law[19], $-\log\sigma = T^{-n}$, was applied to electrical data obtained from isothermal electric experiments performed on samples A, B and C at fixed constant temperatures, before and after the conformational change, according to the procedure described in the Experimental section. They were used to calculate activation energy, E_a, and n values, in order to shed light on the conductor mechanism. The n coefficient takes $n = 1$ for an Arrhenius thermally activated process, $n = 1/2$ for a conduction mechanism suggested for a hopping model with charge transfer occurring by hopping between, along and across conductor chain units[20], and $n = 1/4$ when the hopping process develops among conductor islands separated by an insulator matrix[21]. From n and E_a values given in *Table 2* it is noted that at high temperatures the calculated n values are close to 1/2, corresponding with excessive activation energy values that have not much sense from a quantitative point of view. In our opinion, the fit of our systems to this theory might explain a possible conductive mechanism, by hopping of charge carriers among active sites, which become separated by thermal effects, but it is not admissible due to the high energy required.

At low temperatures, the value of $n = 1$ is consistent with a thermally activated mechanism, and the corresponding E_a values are in the energy range referenced for this kind of conductor process in organic polymers[22]. Moreover, E_a values are in concordance with the explanation above, in the sense that the highest E_a obtained for sample C is in agreement with C-numbered samples being less conductive. The minor E_a value of sample B corresponds to the most conductive, for which $n = 1, 5$ (i.e. $1 + 1/2$), and it could be assumed to be due to the contribution of two simultaneous mechanisms: a thermally activated mechanism, with $n = 1$, and another mechanism of hopping of charge carriers between CTC units, that corresponds to $n = 1/2$.

Table 2 Values of n parameter and activation energy, E_a obtained by applying the Power law[18]

	Low temperatures[a]		High temperatures[b]	
Sample	n	E_a (eV)	n	E_a (eV)
A	1.0	0.52	0.5	20
B	1.5	0.15	0.6	4.7
C	1.0	1.03	0.6	7.8

[a] At 30, 35, 40, 45 and 50°C (before the conformational change)
[b] At 180, 185, 190, 195 and 200°C (after the conformational change)

CONCLUSIONS

The chemical procedures applied are useful to graft tcPc on PVK. Chemical groups involved in this reaction will be of importance for its thermoelectrical response.

Homodispersity has a certain importance in the grafting procedure of A fractions, since grafting low molecular weights presented the highest current density value (and therefore high conductivity) while the graft of its corresponding unfractionated PVK (i.e. sample A) gave a smaller conductivity.

All grafted PVK samples manifested a reversible conformational change, apparent during the application of thermoelectrical treatments.

Results induce to think that polymer segments with hanging aromatic structures require a proper configuration in order to improve conductivity.

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