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ELECTRON SPIN RESONANCE OF SOME CONJUGATED POLYMERS

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In this paper we present simple and qualitative ideas concerning the origin and nature of unpaired electrons which are currently observed on a great variety of conjugated polymers. It is suggested that in almost all cases these unpaired electrons are associated with the presence of structural defects such as cross-links or macrocycles. This statement is favourably compared with experimental results obtained on poly(acetylene) and poly(phenylene) systems. The case of doped materials is also investigated and the particularly important problem of dopant distribution homogeneity through the sample is discussed.

INTRODUCTION

Conjugated polymers have long been the subject of intense experimental [1] and theoretical[2] studies. In the last few years there has been a new interest in these systems, due to the ability of some of them to be brought to metallic level by doping with various chemical species[3]. Because of their molecular conformation, conjugated systems can be the subject of chemical reactions which can induce unpaired electrons whose magnetic properties are easily studied using EPR. At this time magnetic measurements have been performed on a considerable number of conjugated organic materials and a large review of the observed behaviours has been reported[1]. Most of these systems present an EPR spectrum whose characteristics are very similar: a g-value

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close to 2, a spin concentration between 10^{18} and 10^{20} spins/gr, a symmetric shape, without structure generally, with a width between 1 and 10 Gauss [4-21].

In table 1 we present some general features of the electronic resonance observed on the most currently studied conjugated polymeric systems:

1. the existence or absence of an EPR signal close to $g \sim 2$.
2. the peak to peak linewidth ΔH_{pp} of the absorption derivative.

It is observed that many of the pristine materials do not present a significative absorption. On the contrary, after doping with AsF_5, which has been chosen as the most common dopant, almost all the systems show an EPR signal. We also note that the range of linewidth values measured after doping is not fundamentaly changed if compared with the undoped case.

Table 1 Some characteristics of the EPR of selected conjugated polymers.

	pristine		doped		ref.
	EPR Signal	ΔH_{pp} (G)	EPR signal	ΔH_{pp}	
cis-polyacetylene	no	-	yes	2	4,7,9
trans-polyacetylene	yes	.2 to 1	yes	1	4,5,7,,9
polyphenylacetylene	yes	12	yes	?	10,11. 15
poly(1,6heptadyine)	yes	4	yes	4	16
polyphenylene A [a]	yes	5	yes	1	17
polyphenylene B [b]	no	-	yes	4	18
polytoluene [a]	yes	5	yes	4	21
polyphenylene vinylene	no	-	yes	.5	19
polyphenylene sulphide	no	-	?	?	18
polyvinyl chloride	no*	17	?	?	20

[a] polymerized using the Kovacic method[22].
[b] polymerized using the Yamamoto method[23].

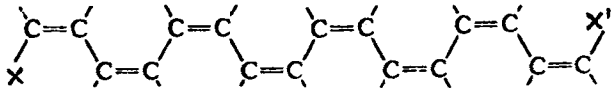
* Yes, after a strong γ rays irradiation[20].

In order to understand these behaviours, we must answer the question of the origin of the unpaired electrons in conjugated polymers. The situation is almost clear concerning the nature of the spins existing in undoped poly(acetylene). But the process by which unpaired electrons are created and stabilized in this material is still a problem. The case is even more difficult for poly(phenylene) for which no hypothesis exists about the observed EPR signal. The case of doped systems has been only slightly investigated and is actually complicated as even the influence of the dopant on the structure, the exact chemical nature of the doping species, its distribution uniformity through the sample are still not well known.

In this paper we present simple and qualitative ideas concerning the origin of the unpaired electrons which are observedin ,undoped and doped, poly(acetylene and poly(phenylene). We show that these concepts are supported by currently obtained experimental results.

THE CASE OF UNDOPED POLY(ACETYLENE).

The polymerization of acetylene (C_2H_2) at low temperature (-78°C) is known [3] to lead to a chain with the cis configuration



where X and X' are saturated terminal groups whose nature will not be discussed here. The main feature of the ideal chain is its even number of Carbon atoms with a consequent absence of unpaired electrons. In such a case we do not expect any EPR signal, as is observed experimentally[7,24]. As thermal isomerization proceeds, the number of unpaired electrons increases with increasing temperature. In order to explain such a fact, we suggest that cross-links appear during the thermal treatment with the consequent creation of trans sequences with an odd number of C atoms (Fig 1a) and unpaired electrons close to the cross-links. Nevertheless, according to Salem [2] and Su[25] such a situation is not stable and the electron must be delocalized towards the center of the trans sequence (Fig 1b). This picture is in total agreement with the soliton model of trans-$(CH)_x$, the electron mobility being thermally activated as evidenced by the strong temperature dependence of the EPR linewidth[3].

The existence of crosslinks in trans-$(CH)_x$ is supported by the following experimental facts:

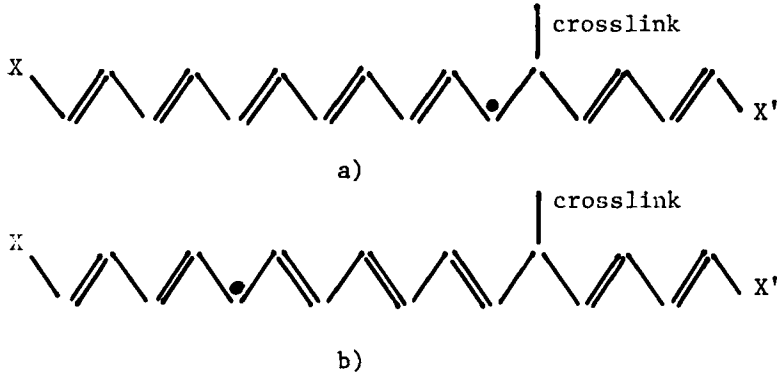


FIGURE 1 Schematic representation of the creation of one unpaired electron related with the existence of a crosslink in an arbitrary position.

1. the activation energy for the degradation of the trans-$(CH)_x$ is rather small ($\sim$30 kcal/mole)[9] compared with the values observed for saturated polymers[26]. Then crosslinks which take place during the degradation process are very likely in polyacetylene even at room temperature.

2. the ability to be stretched is lost during a thermal treatment of cis-$(CH)_x$[3] indicating an increasing amount of crosslinked chains in the sample. These crosslinks could occur in amorphous regions (interconnexion between crystalline fibers for instance) where separations between chains can have favourable values.

3. Raman spectroscopy shows[27] that if cis-$(CH)_x$ is characterized by long polymeric chains, the trans isomer presents a broad distribution of trans sequence lengths, consistent with a random distribution of crosslinks along the chains.

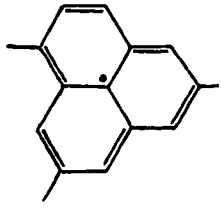
4. finally we note that our simple model predicts an average of one unpaired electron per chain. If we take for the molecular weight a value on the order of 7000 as determined by Shirakawa et al.[28], we obtain 2000 ppm for the concentration of spins in trans-$(CH)_x$, a value in good agreement with experimental determinations from the EPR data which are generally of the order of 1000 ppm[4-9].

5. very recently it has been shown [29] that isomeriza-

tion of cis-$(CH)_x$ induced by electrochemical doping, process which is not expected to introduce crosslinks, gives a trans $-(CH)_x$ with a very small number of unpaired electrons if compared with the trans-$(CH)_x$ obtained by a thermal treatment. This is again consistent with the assumption of un paired electrons correlated with the creation of cross-links upon a thermal treatment.

THE CASE OF UNDOPED POLY(PHENYLENE).

The two systems presented in the table 1 differ by the polymerization procedure. For system (A) the polymerization implies the formation of radicals randomly distributed on the benzene ring [22]. On the contrary, the polymerization of system (B) occurs through the formation of bromine di-substituted benzene and therefore links in para position are thus favoured [18]. In case (A), defects of the following type can be formed



leading to delocalized unpaired electrons [30], whose resonance consists in a structureless single line. The mobility of such electrons is very limited, consistent with the almost temperature independent EPR linewidth [17]. On the contrary no defects of the above type are expected in case (B) as a result of preferential polymerization in the para position. The consequent absence of unpaired electrons is confirmed by the experiment [18].

We finally note that systems like poly(phenylene) [19] and polyphenylenesulphide [18] which are obtained with a method similar to case (B), are also characterized by the absence of a significative EPR signal.

THE CASE OF DOPED POLYACETYLENE.

We consider here only the case of the trans isomer. All the doped samples show important variations of their EPR intensity and linewidth. After doping to the metallic level they also show a typical Dysonian EPR spectrum characterized by the assymetry ratio A/B. This data is reported in Table 2 for various doping species. It is observed that there is

no universal behaviour. Nevertheless all the doping processes are accompanied by a continuous variation of the EPR parameters, number of spins (N_s), and linewidth (ΔH_{pp}). This suggests that the spectra observed after doping arise from unpaired electrons in undoped parts of the sample, whose resonance is only perturbed by the semiconducting or metallic state of the surrounding system. For instance in the case of a rapid iodine doping process, which is known to give a very inhomogeneous distribution of the dopant in the system [31], yields a rapid decrease of N_s which stabilizes at a given value N_s' after a few hours. On the other hand a slow doping procedure, which improves the homogeneity of the sample, is followed by a slow decrease of N_s down to values 2 to 10 times smaller than N_s'. Such results point out the importance of the remaining unpaired electrons in undoped parts of the sample as well as of the kinetics of the doping process.

Table 2 EPR behaviour of doped polyacetylene.

upon doping with	N_s	ΔH_{pp}	A/B	ref.
I_2	↘	↗	2 to 3	7
SbF_5 AsF_5	↗	↘	2.5	5,7.
$NOHSO_4$	↘	↗	6	12
Li Na	↗↘ *	↗↘ *	8 3	11,13.

* the observed evolution depends on the doping time and consequently on the dopant concentration.

The case of AsF_5 or SbF_5 dopants is much more delicate because, in addition to their doping character, they also act as catalyst for the polymerization of acetylene [32]. The observed increase of N_s after doping with these species could then be due to a microstructural modification of the system leading to the creation of new unpaired electrons.

The n-type dopants Li and Na do not give significantly different results. On the contrary very recent results [12,14] point out again the importance of the doping kinetics for the dopant homogeneity in the system.

THE CASE OF DOPED POLY(PHENYLENE).

In case of system (A), doping with AsF_5 induces the same qualitative behaviour as for AsF_5 doped $(CH)_x$: an increase of N_s with a decrease of linewidth ΔH_{pp}. Further comparison with poly(acetylene) is not possible because no other doping species have been studied using EPR on poly(phenylene). We just note that, in the present case, AsF_5 also acts as a catalyst for polymerization of benzene and that microstructural changes during the doping process could occur, leading to the creation of unpaired electrons[33]. In case of system (B) a strong EPR signal appears after doping with AsF_5 (Table 1) whose origin is probably also related to the increase in degree of polymerization induced by the dopant, leading to the formation of macrocycles of the type described above. Further experiments are needed in order to clarify these points.

CONCLUSION.

In this qualitative analysis of some EPR data, we have tried to introduce some simple ideas concerning the origin of the unpaired electrons existing in conjugated polymers. The main conclusions we have pointed out are all based on the assumption that there exists some correlation between intrinsic or introduced structural defects and the existence of spins in these systems:

1. in trans poly(acetylene) these spins would be associated with crosslinks created during the isomerization process or with structural modifications introduced during the doping process.

2. in poly(phenylene) these spins would be localized on macrocycles which are a consequence of the polymerization procedure.

We have also pointed out the extreme importance of the

homogeneity of the system in order to understand the EPR of doped samples and suggested that in the observed spectra a large part comes from unpaired electrons in undoped parts of the material.

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