Magnetic Properties of *cis*- and *trans*-Polyacetylene as Studied by Electron Spin Resonance

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ABSTRACT: Polyacetylene films strongly react with air, when conserved at room temperature and atmospheric pressure. We present here an experimental electron spin resonance (ESR) study on the variation of the linewidth and number of spins with time and temperature of *cis*- and *trans*-(CH)_x films of different thicknesses. It is shown that this evolution is qualitatively and quantitatively different for the two isomers. The number of resonant spins increases with time with a characteristic time of the order of 8 hours in the case of the *cis* isomer. For the *trans* isomer, the number of resonant spins, which is an order of magnitude greater than the final value of the *cis* isomer, is remarkably constant with time while the linewidth and amplitude are not. In the light of these results, the origin and nature of the observed resonant spins are discussed.

KEY WORDS Magnetic Resonance / Polyacetylene / Oxidation / Isomerization /

Polyacetylene is now a material of considerable interest as, upon doping with chemical species as I₂, AsF₅, SbF₅, etc., its electronic transport properties cover the whole range from insulators to metals and semiconductors.¹⁻³ This behaviour is strongly correlated to the intrinsic nature of the polymeric chain which consists of conjugated double bonds in the *cis* or *trans* configurations. As a consequence of this nature, polyacetylene is also very sensitive to oxygen which can considerably change its mechanical,⁴ electrical,⁵ and magnetic properties.^{6,7} Such a fact leads to a complicated situation if one tries to interpret quantitatively the properties of doped systems, as the final measured quantities may or may not strongly depend on the whole history of the sample and particularly the presence of air during treatment. In that sense, it is interesting to investigate the behaviour of undoped polyacetylene

samples in order to determine precisely which type of evolution applies to a given situation.

It is also of interest to investigate the properties of undoped polyacetylene so as to understand the origin of the unpaired electrons which contribute to the observed electron paramagnetic resonance (EPR) signal. For this purpose, the *cis* and *trans* isomers cannot be considered as equivalent. Different authors^{7,8} have postulated the existence of neutral defects in the *trans* isomer, appearing as domain walls or solitons.

This is compatible with the fact that this isomer is energetically unaffected by the interchange of double and single bonds (I),

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But this is not the case for the *cis*-isomer since *cis-transoid* and *trans-cisoid* are not energetically equivalent^{9,10} (II).

This situation normally allows us to predict different behaviours for the two isomers. In fact, this is not generally qualitatively the case at room temperature as is seen from electrical¹¹ and magnetic^{2,6,7} measurements on doped samples. We thus have to make the assumption that in addition to the normal thermal transformation from *cis* to *trans*, any doping process induces some change in the *cis* configuration, as suggested by Chiang *et al.*¹¹

We present here a systematic study, with the evolution of time and temperature and with and without the presence of air, of the magnetic properties of the unstable *cis*-(CH)_x isomer and the stable *trans* isomer, using EPR technics. We show that, starting from the low polymerization temperature (−78°C) at which no unpaired electrons exist on the polymer chains, heating of the samples or/and contact with air causes such spin states to come about. We discuss the origin of this behaviour.

EXPERIMENTAL

Polyacetylene films were obtained by the method described by Ito *et al.*,¹² using the Ti(OC₄H₉)₄ + Al(C₂H₅)₃ homogeneous catalytic system in toluene (with molar ratio of Al/Ti=4), at −78°C. Only the films growing on the vertical surfaces, coated with the catalytic system, of the polymerization reactor are considered in this study. The thickness varied from 20 to 130 μm depending on the time of polymerization.

The as-prepared samples, carefully dried, were conserved under vacuum at −25°C. The *cis*-rich isomer was observed to be stable with time. Isomerization to the *trans* configuration was performed at 200°C. The glass tubes containing the samples under vacuum were directly immersed in isopentane for given time (5 minutes to 2 hours).

One of the samples was directly polymerized at −78°C inside the EPR tube. The tube was sealed

under vacuum the sample being always kept at low temperature. The sample was then immediately introduced in a variable temperature cryostat, stabilized at −78°C, inside the spectrometer cavity.

The electron spin resonance (ESR) spectra were recorded on an ER10 Bruker spectrometer working at 9.0 GHz. The maximum hyperfrequency power was 30 mW. To study the evolution with time in the presence of air, the sample tube was only open at a specified time and the characteristics of the ESR spectra *versus* time were followed until a reproducible behaviour was reached.

All the experiments described here were performed two or three times on different samples prepared at different times to be sure that the observed behaviour was not just a spurious effect.

EXPERIMENTAL RESULTS

The *cis*-Isomer

If observed at the polymerization temperature −78°C the ESR spectrum as described previously¹³ showed no signal from the polyacetylene film while a very huge and broad signal centered near *g*=1.95 came from the catalytic system. Such a catalyst signal has been studied by different authors^{14,15} and a strong dependence of its shape with the molar ratio of Al/Ti was pointed out. Our results are consistent with what is expected for a molar ratio of 4.

Table I. Characteristics of the ESR Lorentzian spectra at room temperature obtained on *cis*-(CH)_x and *trans*-(CH)_x.

The *cis/trans* content was determined using IR and Raman Spectroscopy. The *trans* isomer was obtained from a fresh *cis*-isomer sample kept at 200°C under vacuum during one hour.

	<i>cis/trans</i> Content	Number of spins g ^{−1}	ΔH_{pp}	<i>g</i> Value
			Gauss	
<i>cis</i> -(CH) _x	~95%	~10 ¹⁸	8.0 ± 0.3	2.0023
<i>trans</i> -(CH) _x	~5%	~10 ¹⁹ —10 ²⁰	1.25 ± 0.05	2.0023

Figure 1. Time dependence of the ESR signal intensity of a 95% *cis*-(CH)_x sample exposed to air at room temperature.

Figure 2. The difference between the ESR signal intensities at time t and ∞ , normalized to unity for $t=0$, is plotted in a Log scale versus t , for three 95% *cis*-(CH)_x samples having different thicknesses and submitted to air at room pressure and temperature. If not actually linear, the characteristic times of the observed dependences are quite similar in the three cases (see Table II).

With an increase in temperature, the signal coming from the catalytic system was strongly modified. At the same time, a small symmetric signal started growing at $g=2.0023$, the amplitude of which increased with increasing temperature. At room temperature this signal had an intensity corresponding roughly to 10^{18} spins per g, a width (between the peaks of the absorption derivative) of 8.8 Gauss with a lorentzian shape (see Table I). Opening the tube to air at room temperature was shown to produce a great decrease in catalyst signal while the (CH)_x signal continued to grow. We observed that the amplitude $A(t)$ of the spectra at time t increases rapidly just after the opening to air and saturates to a constant value $A(\infty)$ after a few days (Figure 1) corresponding to an increase of approximately one order of magnitude in the number of unpaired electrons. On the other hand the line width ΔH_{pp} does not change significantly at the time scale of three days.

The quantity $A(\infty) - A(t)$ represents the deviation from equilibrium of the ESR amplitude at time t . On Figure 2 we have plotted $A(\infty) - A(t)$ in log scale versus t , for samples of various thicknesses. The observed variation is not actually linear. Nevertheless we can deduce a rough characteristic time of the order of 8 hours for the evolution of $A(t)$, which is observed to be independent on the sample thickness (Table II).

After more than three days at room air and temperature, the tubes containing the *cis*-(CH)_x samples were sealed under vacuum and kept at

Table II. Characteristic time of the evolution of the number of spins for a *cis*-(CH)_x samples submitted to air at room temperature, with three different thicknesses

Thickness	Characteristic time
	min
20 μm	480 ± 90
30 μm	390 ± 60
130 μm	480 ± 60

200°C for one hour in order to change the configuration from *cis* to *trans*. After that the ESR spectra showed a strong increase in intensity (between $\times 10$ and $\times 100$ depending on the starting value of the *cis*-isomer) while the linewidth ΔH_{pp} decreased to a value of 2.5 Gauss. This value was obtained for various samples and seems to be a universal limit correlated with the type of treatment on the sample.

This value should be compared with the value $\Delta H_{pp} = 1.25$ Gauss for the *trans* isomer prepared from the *cis* isomer which had no contact with air.

The *trans*-Isomer

The *trans* configuration was obtained from the *cis* one by heating the sample for one hour as described above. The characteristics of the ESR spectra are summarized in Table I. We observed a strong increase in the unpaired-electrons density while the linewidth decreased. Kept under vacuum at room temperature, the characteristics of the spectra of these samples do not change with time.

If the sample is subjected to air at room-atmospheric pressure, we note change in the ESR spectra quite different from those observed on the *cis* isomer. The amplitude of the signal slightly decreases while its width increases up to 2.6 Gauss (Figure 3). A stationary situation was attained after roughly two days. Nevertheless during the whole evolution the number of unpaired spins remained constant except for a slight decrease which occurred at the very beginning.

We must note that the stationary value for the linewidth obtained in this case is approximately the same as the one observed for a *cis* isomer first subjected to air and after being isomerized to the *trans* configuration. This suggests that the final stationary situation (oxidized *trans* configuration) obtained in the two cases does not depend on the manner to reach it.

Figure 3. Time dependences of the ESR characteristics of a 95% *trans*-(CH)_x sample exposed to air at room temperature: (1), amplitude normalized to unity for $t=0$; (2), linewidth in Gauss; (3), number of unpaired electrons normalized to unity for $t=0$.

Figure 4. Neutral defect appearing in the *trans* configuration as a consequence of dephasing in the bond alternation: a, localized defect; b, delocalized defect spread over a given number of C atoms, or domain wall.

DISCUSSION

The absence at low temperature of any signal on the *cis* isomer indicates that no neutral defects involving unpaired electrons exist in the case of *cis* configuration. This is compatible with the fact stated above that the two distinct geometries of this configuration are not energetically equivalent and this situation does not favour the existence of defects in the double-bond alternation. On the other hand the high density of unpaired electrons observed with the *trans* isomer is consistent with the existence of neutral defects of the type proposed by Chiang *et al.*¹¹ and Goldberg *et al.*⁶ (Figure 4), which is in agreement with the two energetically equivalent geometries of this isomer.

Between these two limiting cases, any intermediate situation, obtained as well by heating the *cis* isomer as by submitting it to air, must be understood in terms of partial isomerization.

The heating of the pure *cis*-isomer was shown¹³ to create unpaired electrons whose resonance *g* value could not be distinguished from the free electron value.

The width of the observed spectra decreases when the *trans* content of the samples increases, as first shown by Shirakawa *et al.*¹⁶ Such a width has its origin partially in unresolved hyperfine interactions as stated by Snow *et al.*⁷ who compared the cases of (CH)_x and (CD)_x systems. We confirmed this conclusion, since spectra obtained on ¹³C enriched samples have all show widths larger than the

Table III. Values of the linewidth ΔH_{pp} of the ESR spectra obtained on the *cis* and *trans* isomer of the different undoped samples

	95% <i>cis</i>	95% <i>trans</i>
(CH) _x	$\Delta H_{pp} = 8 \pm 0.3$ Gauss	$\Delta H_{pp} = 1.25 \pm 0.05$ Gauss
(CD) _x	$\Delta H_{pp} = 3.2 \pm 0.2$ Gauss	$\Delta H_{pp} = 0.7 \pm 0.05$ Gauss
(¹³ CH) _x 50%	$\Delta H_{pp} = 14.4 \pm 0.5$ Gauss	$\Delta H_{pp} = 2.5 \pm 0.2$ Gauss
(¹³ CH) _x 90%	$\Delta H_{pp} = 17 \pm 0.8$ Gauss	$\Delta H_{pp} = 2.9 \pm 0.4$ Gauss

corresponding non enriched systems (Table III).

Weinberger *et al.*¹⁷ attempted to simulate numerically the ESR line for *trans*-(CH)_x assuming that the width could be attributed entirely to unresolved hyperfine splitting, as a consequence of spin mobility. At 4.2 K, a fit with their experimental data involved such a mobility over 30 to 40 carbon atoms along the chain. At room temperature, this mobility is expected to be considerably higher, as evidenced by the decrease in ΔH_{pp} with increasing temperature.⁶ Therefore the larger width observed with a great *cis* content can be interpreted as follows. The *trans* content at room temperature for what we call our *cis* isomer is of the order of 5%. This amount

was isomerized quite rapidly when the sample heat from its polymerization temperature to room temperature.¹³ Consequently, we suggest such an amount to be located on chain ends where the ability to rotate around C–C bonds is greater than in the middle of the chain. Using $n=1000$ as a mean value of the number of carbon atoms in one chain, as estimated by Shirakawa *et al.*,¹⁸ we then obtained *trans* sequences consisting of 25 carbon atoms. With the model proposed by Weinberger *et al.*,¹⁷ unpaired electrons associated with *trans* sequences of such an extent would give an ESR spectrum width of ~ 6 Gauss which is compared reasonably with our experimental value of 8 Gauss (Table I), taking into account the crudeness of the assumptions model. This indicates that even at low temperature, a model assuming defects of relatively high mobility, which are intrinsic characteristics of the *trans* configuration, is consistent with the existing experimental data.

A study of the effect of air exposure allows us to gain further understanding of the magnetic properties of undoped samples. Snow *et al.*⁷ have studied the effect of oxygen on the characteristics of the ESR spectra. Nevertheless, a clear distinction between the *cis* and *trans* isomer cases was not made, leading to inaccurate conclusions concerning the observed behaviours. Goldberg *et al.*⁶ have also studied oxygen effects on the *trans*-isomer and have suggested the existence of a weak interaction of the chains with oxygen, followed by a slow chemical reaction. Our more detailed results obtained on the *trans*-isomer allow us to precise the following:

(i) The constant intensity of the ESR spectra during exposure to air indicates that no more unpaired electrons are induced by interaction with oxygen (Figure 4).

(ii) Nevertheless, an increase in linewidth (Figure 4) by a factor of ~ 2 is due to a reduction in spin mobility due to the presence of oxygen.

It is easy to understand these points if we suppose that oxygen interacts with the system as a diamagnetic O_2^{-2} species whose effect is only to create along the chains static-defects which limit the extent of mobility of the observed spins, leading to an increase in ΔH_{pp} . Such a chemical species, which can be considered as a partial cross-linking agent is likely in $(CH)_x$ as exposure to air is known to very rapidly damage its mechanical properties,¹⁹ and stretchable films become brittle.

Coming now to the *cis*-isomer case, the experimental results described above lead to the following conclusions.

(i) The presence of oxygen creates paramagnetic centers whose characteristics are the same as those of the starting unoxidized system.* (g value, linewidth and absence of hyperfine structure of the ESR spectra are similar before and after oxidation).

(ii) The constant value observed for the characteristic evolution time (Table II) of the signal intensity suggests that we are concerned with a diffusion process which does not depend on sample thicknesses.

This last point is consistent with the fibrous structure of $(CH)_x$ which allows a rapid diffusion inside the sample between the fibrils.

A further evolution is then due to diffusion in the fibrils themselves whose size does not depend on the sample thickness. This conclusion is in contradiction with a recent model proposed by Rice and Timonen²⁰ who suggested that any doping species was more or less (depending on its molecular volume) restricted very near the surface of the fibrils. Nevertheless if interpreted in terms of molecular oxygen diffusion, the observed behaviour of Figure 3 would give a diffusion coefficient as low as $10^{-16} \text{ cm}^2 \text{ s}^{-1}$. Even if we invoke the high crystallinity of the fibrils,²¹ which generally restricts diffusion, the above value seems very small compared with other types of semicrystalline polymers.²² Thus it seems reasonable to suppose that the effect of oxygen is to increase the rate at which the *cis* configuration transforms to the *trans* one. Diamagnetic O_2 molecules by breaking double bonds along the chains, make rotation around C–C bonds. The consecutive increase in *trans* content, which has been observed by infrared (IR) spectroscopy,²³ then appear as an increase in unpaired electrons. The fact that the linewidth does not change significantly during the intensity evolution indicates that the *trans* sequences created have an extent comparable with that obtained during the only thermal isomerization. This suggests a strong similitude between the effects of oxidation and thermal isomerization. This point is supported by the fact stated above that thermal isomerization fol-

* We must remind that the unoxidized *cis* system has at room temperature a *cis* content of 95% and that the ESR signal comes from the remainder 5% of *trans* isomer.

lowed by oxidation leads to the same final situation (*trans*-isomer with $\Delta H_{pp} \sim 2.5$ Gauss) than oxidation followed by thermal isomerization.

CONCLUSION

We have shown that the characteristics of the observed ESR spectra are governed by the *trans* content of the samples. Starting from the pure *cis*-isomer, for which no ESR signal is observed, thermal isomerization causes unpaired electrons to appear. At a given temperature, the effect of oxidation increases during a certain time (a few days at room temperature) the rate at which isomerization proceeds. Additional experiments are needed for analyzing quantitatively the characteristics of the neutral defect which have been used for interpreting our experimental results.

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Note Added in Proof. Very recent results obtained by S. Lefrant *et al.*,²⁴ using Raman spectroscopy, clearly show that oxidation of a *cis*-(CH)_x sample largely increase the rate (at room temperature) at which isomerization occurs, in agreement with our present conclusions.

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