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Dielectric properties of undoped polyacetylene films in a large frequency range

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Résumé. — Des mesures diélectriques ont été faites dans un intervalle étendu de fréquences (10⁻⁴-10⁺⁵ Hz) sur des échantillons non dopés de cis-polyacétylène provenant de différents laboratoires, en utilisant à la fois des contacts ohmiques et bloquants. La densité de porteurs est faible (2 x 10¹⁶ cm⁻³) et constante; par contre la mobilité est thermiquement activée, avec une énergie d'activation qui dépend des échantillons et des contacts. Dans le cas de contacts bloquants et sur les échantillons les moins conducteurs (5 x 10⁻¹² 0³A⁻¹ cm⁻¹), on a trouvé une énergie d'activation maximum d'environ 1,6 eV.

Abstract. — Dielectric measurements were performed in a large frequency range (10⁻⁴-10⁺⁵ Hz) on undoped cis-polyacetylene samples from several laboratories both with ohmic and blocking contacts. The carrier density is low (2 x 10¹⁶ cm⁻³) and constant but the mobility is thermally activated with a sample and contact dependent activation energy. A maximum activation energy of about 1.6 eV has been found with blocking contacts on the less conducting samples (5 x 10⁻¹² 0³A⁻¹ cm⁻¹).

1. Introduction. — The remarkable electrical properties of films of doped polyacetylene have been extensively investigated [1-5]. The semi-conducting behaviour of light doping (below one percent) has been clearly established from the possibility of formation of heterojunction and Schottky diode [6-10]. However the transport properties of undoped and doped (CH)x are not clearly understood. Different models have been developed as, for example in the soliton formalism, the hopping conduction [11] or the formation of metallic regions in the surrounding « insulating » medium[12]. In such a disordered system (fibrillous nature, eventual inhomogeneity of the doping, interfibrillar contacts, chemical defects in the chains and impurities), the experimental results depend on the nature of the samples (bulk compacity, thickness of the film, the detail of the polymerization process) i.e. the nature of all the defects. The characterization of these defects needs a detailed study of the transport properties. In particular the dielectric properties of the pristine and lightly doped (CH)x have only been the aim of a few papers [13-15]. The average dielectric constant at microwave frequencies was found to be 4.0 for trans-(CH)x and 3.4 for cis-(CH)x, the value depending on the samples (oriented by rolling, low density or pressed) [14, 15]. The frequency dependence of the complex conductivity for different doping levels has shown that the trans-(CH)x films seem much more homogeneous than would be expected in this kind of disordered material [13].

This work deals with the complex dielectric permittivity measurements in the low frequency range (10⁻⁴-10⁵ Hz) of pristine cis-(CH)x during the isomerization process at different temperatures and on samples from different laboratories with different thickness and apparent density [16]. Results concerning both ohmic and blocking contacts show a strong sensitivity of behaviour to the density of samples and to the polymerization process; the role of residual oxygen is invoked. The transport properties are interpreted in terms of a constant carrier density with an activated mobility. Data concerning the trans-(CH)x are compared to those reported by Grant and Krounbi [13]: these authors did not find dispersion effects on the trans-(CH)x samples with ohmic contacts nor non linear effects with high applied fields. These points will be discussed.

2. Experimental conditions. — The polycrystalline films are all prepared by the method developed by Shirakawa [17]. Samples have been obtained from different laboratories (for notation see note [16]). The
CRM samples have been synthesized in a reactor described elsewhere [18]. Before use, all the samples were maintained in sealed tubes. They were metallized in vacuo (10^{-6} torr). All sample handling was carried out in the inert atmosphere of a dry box with the exception of a very short air exposure during a few minutes (from sealed containers to the evaporation device and then to the measuring cell).

In the determination of the dielectric properties of the pristine cis-(CH)_x, one must be aware of two difficulties: the thermal isomerization and the presence of impurities. At room temperature the pristine cis-(CH)_x films contain about 85% cis sequences. While heating, isomerization takes place and the cis content can be evaluated from the results reported by Ito et al. [30]: after 5 hours the cis content is 60% at 75 °C, 45% at 85 °C, 30% at 95 °C, 18% at 105 °C and films are nearly all trans at still higher temperatures. Note that time needed for our measurements at one temperature is about 3 hours. After thermal treatments up to 85 °C, the dielectric properties at room temperature are unchanged and may be considered as characteristic of the cis-(CH)_x. The narrow temperature range between this temperature (85 °C) and the minimal temperature allowed by the sensitivity of the technics (about room temperature), makes the determination of an activation energy inaccurate.

The second difficulty concerns the presence of at least two kinds of impurities, oxygen and the unremoved catalyst. They are both present in any pristine film but at a low concentration, as can be seen directly for the catalyst through chemical analysis, atomic spectroscopy (less than 0.2 molar percent for Ti) and the retrodiffusion technics [31]. The residual oxygen content (less than 0.2 molar percent) in (CH)_x films has been evaluated by compensation with a n-type doping (benzophenone-disodium) [18].

The dielectric measurements (G_p parallel equivalent conductance and C_p parallel equivalent capacity) were made in vacuo (10^{-5} torr) with a conventional bridge between 10^2 and 10^5 Hz and with an automatic apparatus made in our laboratory in the range 10^{-4}-10^2 Hz [19].

The corresponding DC I(V) curves were also recorded. Various geometrical arrangements were used: bulk currents through the sample or surface currents between electrodes (1 mm apart) were recorded. Furthermore some implantation experiments, similar to those already reported by Allen et al. [20] were made and will be discussed elsewhere.

3. Experimental results. — The experimental results are very different with aluminium and gold contacts, whatever the samples. Au contacts are always ohmic in AC or DC current (up to 80 V applied). Al contacts are blocking and Schottky barriers can be expected, as observed for In [13, 21] on account of their similar work functions [22].

3.1 Al ELECTRODES. — A very large relaxation is observed in the very low frequency (VLF) or low frequency range in all the samples. For example on figures 1 and 2, G_p and C_p are plotted versus frequency for two CRM samples of thickness 200 and 400 µ. Different regimes may be distinguished in the

![Graph of Equivalent parallel conductance and capacity versus frequency G_p(ω) and C_p(ω) respectively, of a CRM sample of thickness 200 µ. Measurements have been performed with aluminium contacts of contact area ~ 3 mm² and at different temperatures : (1) 38 °C, (2) 63 °C, (3) 76 °C, (4) 98 °C, (5) 116 °C.](image)

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Fig. 2. — a) $G_p(\omega)$ and $C_p(\omega)$ versus frequency of a CRM sample of thickness 400 µ with aluminium contacts at different temperatures : (1) 26 °C, (2) 46 °C, (3) 57 °C, (4) 83 °C. b) Curve $I(V)$ of the same sample at different temperatures : (1) 26 °C, (2) 43 °C, (3) 57 °C.

Fig. 3. — Tan $\delta$ versus frequency for different samples and temperatures : Al contacts CRM (200 µ) (1) 38 °C, (2) 63 °C, (3) 76 °C, (4) 98 °C. CRM (400 µ) (5) 26 °C, (6) 55 °C. LCM (200 µ) (1') 156 °C. Curve (7) obtained for a fully trans-(CH)$_x$ with In contacts is reproduced from reference [13]. Au contacts (a) CRM (200 µ) at 20 °C, (b) LCM (200 µ) at 156 °C, (c) PHIL at 20 °C.

We turn now to the behaviour of $C_p$. In the very low frequency range a high plateau value of $C_p$ is seen, hardly depending on sample and temperature. In the high frequency range we almost obtain an asymptotic « $C_{oo}$ » value which is sample dependent but temperature independent : the corresponding permittivity $\varepsilon_{oo}$ does not strongly depend on the cis/trans ratio (since films maintained a few hours at 115 °C are nearly fully isomerized [26, 30]).

The $I(V)$ curves are highly non linear, whatever the sample. A threshold near 0.6 V is seen, the slope of Log $I$ versus Log $V$ is nearly 2 in most cases.

3.2 Au electrodes. — On figure 4, $G_p$ and $C_p$ are given versus frequency for some samples and the curves $I(V)$ are ohmic up to 80 V. The plateau of $G_p$ is much more extended towards the low frequencies than in the case of blocking contacts; nevertheless a relaxation is seen from $C_p$ measurements in all samples; it is weaker for the compact ones. The conductivity is much higher than with Al contacts and its activation energy is lower. Compact samples are more conductive with a lower activation energy.

Fig. 4. — $G_p(\omega)$ and $C_p(\omega)$ versus frequency with Au contacts for different samples : CRM (200 µ) (1) 36 °C, (2) 82 °C, (3) 96 °C, (4) 116 °C and PHIL (a) 20 °C, (b) 76 °C.

In the high frequency range, $G_p$ becomes frequency dependent, even in the case of compact samples. When $V > 80$ V, the $I(V)$ curves become highly non ohmic. Between 80 and 100 V (thickness ~ 200 µ) the current increases very steeply with voltage and when $V > 120$ V one cannot obtain a constant current value. Intensity increases slowly with time, sometimes « relaxation » phenomena appear (increase and then decrease of intensity) and sometimes the sample is damaged and disrupted.

We studied trans samples with both kinds of electrodes for comparison with cis-(CH)$_x$ and with the results already published for a narrower frequency range by Grant and Krounbi [13]. Results shown in figure 5 concern only the LCM samples. Finally, different electrode geometries seem to have no influence on the dielectric results : the relaxation with in-plane surface electrodes for PHIL samples is shown on figure 6; the curves have the same general aspect as in the sandwich geometry.

4. Discussion. — Many authors pointed out the influence of contacts on conductivity. For instance Kwak et al. [23] recommend a direct polymerization of (CH)$_x$ on Pt to obtain the « best » contacts. Never-
Fig. 5. — Comparison between dielectric spectra of two LCM samples in the high temperature range in which the sample is nearly fully isomerized to trans-(CH)x: Al contacts (1) 156 °C, (2) 186 °C; Au contacts (3) 156 °C. Note that in the VLF range the capacity values are not very accurate for ohmic contacts : of the order of half a decade for the point near 10⁻³ Hz.

Fig. 6. — Surface property measurements with the PHIL compact sample between two parallel in-plane electrodes 5 mm long and 1 mm apart at room temperature. (a) Gp(ω) and Cp(ω) versus frequency with Al contacts. The dielectric spectrum has the same general features as in the sandwich geometry, the activation energy is smaller. (b) Curve I(V), with (1) Au contacts, (2) Al contacts.

The results concerning blocking and ohmic contacts will be discussed successively.

4.1 WITH BLOCKING CONTACTS. — We can compare the results on cis- and trans-undoped (CH)x. Most of results are on mainly cis-(CH)x samples (see above experimental conditions) and the results of Grant and Krounbi [13] are on all trans samples. Cis-(CH)x shows a very high tan δ peak for the various samples used in our measurements : tan δmax ~ 10 in a large temperature range and whatever the activation energy may be. In the doped trans-(CH)x the same behaviour can be observed but with a much lower value of tan δ. From the results of figures 1 and 2 of reference [13] we can derive the curve 7 of figure 3 with a much lower value of tan δmax ~ 4.5 x 10⁻² ; this value does not depend on doping concentration though the corresponding ωmax varies with the nature of the dopant (O₂ or AsF₅).

In the same way, heating of cis-(CH)x samples for a sufficiently long time allows the transition from the first (high tan δmax value) to the second behaviour (low tan δmax value) with a broadening of the peak for a cis-trans mixture (Fig. 3).

In both cases (cis or trans samples) the plateau capacity in the very low frequency range, or in the low frequency range, is only slightly dependent on temperature or impurity content.

What is the mechanism of this low frequency relaxation ? Classical space charge theories with blocking electrodes and one mobile carrier without recombination [24] give:

$$\frac{C_{st}}{C_{oo}} \simeq \frac{L}{L_D} = m. L$$

is the thickness of the sample, L_D the Debye length, C_st the capacity of the plateau at very low frequencies, C_oo the capacity in the high frequency range. On the other hand tan δmax = 1/2√m and ωmax = ωREL 1/√m

where

$$ω_{REL} = \frac{G_0}{C_oo}, G_0$$

is the plateau conductance. L_D and the carrier concentration N can be evaluated from m. In the case of blocking contacts, the following relation has been established [32] :

$$L_D = \left(\frac{ekT}{2 Ne^2}\right)^{1/2}$$

where ε is the macroscopic dielectric constant which can be evaluated from the capacity at high frequencies. k and e the usual constants and T the temperature.

The values of m derived from tan δmax and ωmax are consistent : for instance, from curve 4 (Fig. 3) we obtain m₁ = 200 whatever the temperature may be. However the value of m from C_st/C_oo is much higher : m₂ between 5 x 10³ and 10⁴. These two values are independent of temperature. From m₂ we obtain N ≪ 2 x 10¹⁶ cm⁻³ and the m₁ value would give a much lower concentration. Both values, which characterize a partly isomerized cis-(CH)x,
are significantly smaller than the corresponding value from thermopower and heterojunction measurements in \( \text{trans-(CH)}_x \), i.e., \( N = 2 \times 10^{11} \text{ cm}^{-3} \) [3]. According to the E.S.R. studies [18], the thermal isomerization from \( \text{cis} \) to \( \text{trans} \) drives the formation of a high concentration in localized states.

This classical theory is not sufficient to account for the dielectric behaviour of the samples. At very early times the carriers accumulate in a thin sheet near the electrode; then a slower mechanism takes place which is not very different in \( \text{cis} \) and \( \text{trans} \) samples (compare figures 2 and 5). This phenomenon is almost the same in the planar and sandwich geometries, the relaxation times being of the same order of magnitude in both cases (Fig. 6). Shallow surface states with a constant density and different time constants (depending on electrode, compacity, polymerization and \( \text{cis}/\text{trans} \) ratio) are likely to be the source of carriers in the blocking case, when a small AC voltage is applied.

In both mechanisms, either classical charge space theory or shallow surface states, the number of available carriers does not depend on temperature since either \( m \) or the low frequency capacity is constant. Only the mobility through the bulk is activated. The same behaviour has been reported for the \( \text{trans-(CH)}_x \) in the light doping regime [3]. These authors argue three possible mechanisms to obtain an activated mobility: 1) the disorder in the polymer which is in appropriate for both \( \text{cis} \) and \( \text{trans-(CH)}_x \); 2) the soliton doping mechanism which is consistent with the transport properties of the \( \text{trans-(CH)}_x \) but cannot be invoked in \( \text{cis-(CH)}_x \); 3) the observed activation energy is the result of inter fibril contact resistance. As the value of the activation energy is insensitive to the nature of samples, this mechanism may be ruled out for \( \text{trans-(CH)}_x \) [3]. In the case of \( \text{cis-(CH)}_x \), we observe a spread of the activation energies (and other characteristics of the transport properties) depending on the samples (compact or not, different thicknesses) and the third mechanism may be argued, the nature of the barriers being undetermined. Models based on metallic domains embedded in a dielectric [12, 25] lead to thermally activated carriers and are not consistent with the present results concerning the undoped \( \text{cis-(CH)}_x \).

The available experimental results have been obtained with ohmic electrodes and give an activated conductivity with an activation energy \( \sim 0.3 \text{ eV} \) in \( \text{trans} \) samples and \( \sim 0.5 \text{ eV} \) in \( \text{cis} \) samples. Our measurements with blocking contacts give higher activation energies, up to \( E_a \sim 1.6 \text{ eV} \) (Fig. 1). This value is quite close to that of the direct energy gap which can be evaluated from the visible absorption of the undoped \( \text{cis-(CH)}_x \), the maximum of absorption being at about 2.1 eV [27], but the coincidence between both values (direct energy gap and limit of activation energy) is likely to be fortuitous since only the mobility is activated. Furthermore the activation energy of the mobility may be overestimated and partly due to the isomerization.

The lowest conductivity and carrier concentration with the highest activation energy have been obtained with blocking contacts for the CRM samples with a thickness which does not exceed 200 \( \mu \). The figure 2 pertains to a thicker sample obtained with a longer polymerization time and a higher monomer pressure. The capacity plateau has the same value as in figure 1, but the activation energy is lower (0.6 eV). The maximum of \( \tan \delta \) has the same value ( \( \sim 10 \) ) but the peak is shifted to higher frequencies. The decrease in activation energy can be due to a more compact structure or perhaps to a weak oxidation. The width of the barrier and the blocking parameter \( G_0/G_{\text{VLF}} \) are decreased (\( G_0 \) is the plateau capacity and \( G_{\text{VLF}} \) is the conductivity in the very low frequency range). More measurements are necessary to give detailed values of every possible activation energy and a detailed interpretation of the data.

With a high DC voltage, the contacts are rectifying and behave like Schottky diodes. However with voltages higher than 80-100 V, the non linearities increase, before an avalanche and disruptive process takes place. By halogen implantation and further evaporation of Al, ohmic contacts with Al are obtained.

4.2 WITH OHMIC CONTACTS. — Some measurements with AC or DC on undoped \( \text{trans} \)- or \( \text{cis} \)-polyacetylene samples with gold contacts have been reported [1, 28]. However the results are as yet dispersed.

From Chiang \textit{et al.} [2] the undoped \( \text{cis} \) isomer is less conducting than the undoped \( \text{trans} \) isomer (\( 2 \times 10^{-9} \text{ } \Omega^{-1} \text{ cm}^{-1} \) and \( 2 \times 10^{-5} \text{ } \Omega^{-1} \text{ cm}^{-1} \) respectively). However it has been shown that the thermal isomerization induces large amounts of defects [18].

Pochan \textit{et al.} [28] studied the behaviour of 90\% \( \text{cis} \) samples with Au electrodes at 1 000 Hz. They report a constant dielectric permittivity of about 2-3 up to the room temperature and an abrupt increase near 310 K. The \( \tan \delta \) increases by 3 orders of magnitude from 10^{-3} at low temperature up to a value of about 1 at room temperature.

With CRM samples (Fig. 4) we obtain higher \( \varepsilon' \) values (between 3 and 6), an activation energy of \( \sim 0.52 \text{ eV} \), a conductivity of \( 2 \times 10^{-9} \text{ } \Omega^{-1} \text{ cm}^{-1} \) at room temperature and a \( \tan \delta \) value of \( \sim 1 \) (at 1 000 Hz). This last value is in agreement with that reported by Pochan \textit{et al.} [28]. Note that the conductivity of the compact PHIL samples is higher (\( 2 \times 10^{-8} \text{ } \Omega^{-1} \text{ cm}^{-1} \)).

It is perhaps more significant to compare samples with Au and with Al electrodes. The plateau conductivity is much higher with Au electrodes and usually \( G_0(\text{Au}) > 1 000 \). The activation energy of conductivity with ohmic contacts is also much lower than that with blocking contacts. In fact, with Au contacts, the carriers (holes) are not "intrinsic" but injected...
by the electrodes. When the injection is high (good ohmic contacts) the deep traps in the sample are no longer empty and the conduction occurs mainly via shallow traps. The evaporated contacts are never perfect and a relaxation of $e^r$ is always present, weaker with compact samples, corresponding to surface states in bad contact with the electrodes. Better contacts can be made by direct growth of (CH)$_x$ on metal [23].

With the injecting Au-(CH)$_x$ contacts, the curves $I(V)$ in DC measurements are ohmic up to an electric field $E \sim 8 \times 10^3$ V/cm. With higher fields, non linearities appear, and the apparent resistance decreases. Similar non linearity effects have been studied in semi-conducting [25] and metallic [1] polyanetylene. Grant and Krounbi [13] studied the non linearity behaviour in AC conductivity at low frequencies up to $10^3$ V/cm with Au contacts. They did not find any non linearity effect in good agreement with our DC measurements; in their case the applied field was too low. H. A. Pohl predicted [29] non linearities with low fields (< $10^3$ V/cm). In fact non linearity appears with higher fields, and several mechanisms have been put forward to explain the mechanism: an avalanche process initiated by high field in the vicinity of electrodes (however the behaviour with high fields is similar and non linearities are obvious with Al and Au electrodes), or a percolation mechanism between small metallic regions [12, 25]. In fact this effect is not clearly understood and comparative measurements are yet to be made in cis and trans samples with various compacities, thicknesses and electrodes. With $E > 2 \times 10^4$ V/cm and Au electrodes, the samples are often disrupted.

5. Conclusion. — Dielectric measurements in undoped polyacetylene samples induce the following conclusions:

— The activation energy of AC conductivity depends on contacts, density and polymerization process.
— With blocking Al contacts, a wide range of activation values (from 1.6 to 0.6 eV) can be found, the carrier density of holes has a constant value, and only the mobility is activated. The value of 1.6 eV has been obtained for the CRM 200 μ thick samples which are the less conducting samples with $\sigma = 5 \times 10^{-12} \Omega^{-1} \text{cm}^{-1}$. These values may be considered as nearly characteristic of the undoped cis-(CH)$_x$.
— With ohmic contacts, the carriers are injected holes, the activation energy is lower (0.5 to 0.3 eV chiefly depending on compacity and structure).
— Dielectric spectra are very similar for sandwich and in-plane geometries.
— Al contacts show a Schottky behaviour.
— Non linearities appear with Au ohmic contacts and electric fields higher than $8 \times 10^3$ V/cm.

All these results are to be supported by further measurements and can afford very important clues to the transport processes in undoped polyacetylene.

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References

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[16] We used samples from various laboratories: Laboratoire de Chimie Macromoléculaire, Université du Languedoc, Montpellier (ref. to « LCM »); Department of Chemistry, University of Pennsylvania, Philadelphia (ref. to « PHIL »); Centre de Recherches sur les Macromolécules (C.N.R.S.), Strasbourg (ref. to « CRM »).


[31] DAVENAS, J., Private communication.