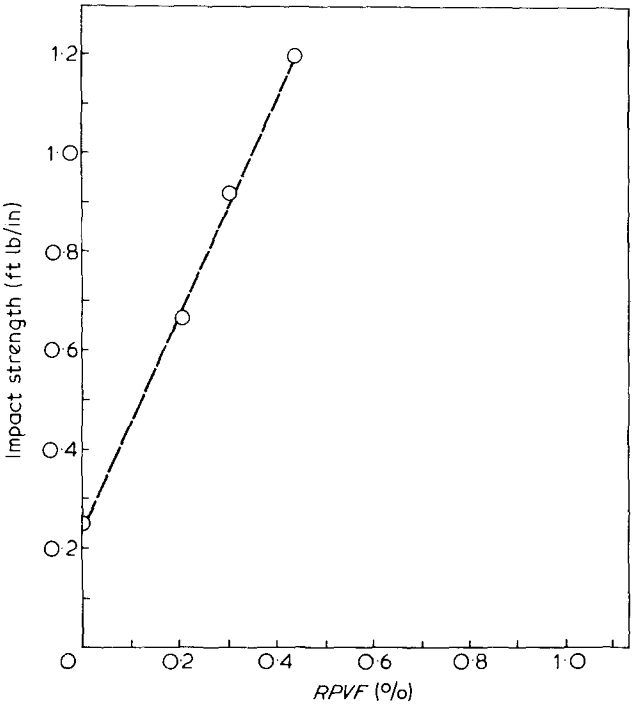

Figure 2 Impact strength vs. *RPVF*

$$(\text{Impact strength} \pm 0.062)\ \text{ft lb/in.} = (12.28 \pm 1.10) \times \log \text{decrement} + 0.094\ \text{ft lb/in.} \qquad (2)$$

Again, the plot is significant to greater than the 99.95th percentile.

Thus, it is clear that here, too, impact strength and dissipation factor correlate well when evaluated under equivalent conditions. This, together with the findings that impact strength and log decrement are linearly related to the volume of the rubber phase, indicates that the assumptions made for homogeneous polymers[3] are true for these heterogeneous polymers, as well: impact strength is imparted by an energy dissipation mechanism at the temperature and frequency of the impact. The ability for such a mechanism to dissipate impact energy is volume-related.

One should, however, not lose sight of the fact that these correlations are empirical. Further work needs to be done to better understand the reasons for their existence.

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Raman study of oxygen induced isomerization of $(CH)_x$ films

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Polyacetylene, $(CH)_x$, is the simplest organic polymer with attractive conduction properties. Doping $(CH)_x$ with appropriate dopants can change its conductivity markedly giving properties covering the whole range from semiconductor to metal[1]. Nevertheless, great care has to be taken, particularly to avoid any contact with oxygen since some properties are dramatically affected by oxidation: conductivity can be drastically reduced upon exposure to air[2]. Oxidized samples have also been reported to have quite poor mechanical properties (no possibility of partial stretching[3]) and finally can be doped to much lower efficiency than fresh samples.

Recent e.p.r. experiments[4] carried out during isomerization of an initially *cis*-film were interpreted by assuming that the e.p.r. signal was due to defects in the double bond conjugation of *trans* sequences. Following this hypothesis, two main points appear clearly: (i) oxidation of a *cis*-sample induces a partial *cis–trans* isomerization; (ii) oxidation of a *trans* sample leads to some extent to a decrease in the length of *trans* sequences in the chains.

Here we describe Raman scattering experiments showing the behaviour of $(CH)_x$ films when exposed to air, in order to check the validity of the above hypothesis. Raman spectra of $(CH)_x$ are well known[5–7] for both *cis*- and *trans*-isomers. The main purpose of these experimental measurements is to follow unambiguously the *cis–trans* content in the films, which is of great importance here. Experimental conditions have been chosen so that Raman spectra of reasonable intensity can be recorded for both isomers, i.e. an exciting wavelength in the red range, 600 nm. The Raman spectrum of the *cis*-$(CH)_x$ is composed of three strong and sharp lines at, respectively, 908 (A), 1247 (B) and 1541 (C) cm^{-1}. For the *trans*-isomer, two broad bands are observed at 1080–1120 cm^{-1} (A′) and 1450–1540 cm^{-1} (B′) of which maxima appear at 1080 and 1450 cm^{-1}, respectively, for the wavelength used[7]. Samples were immersed in liquid nitrogen and the incident power

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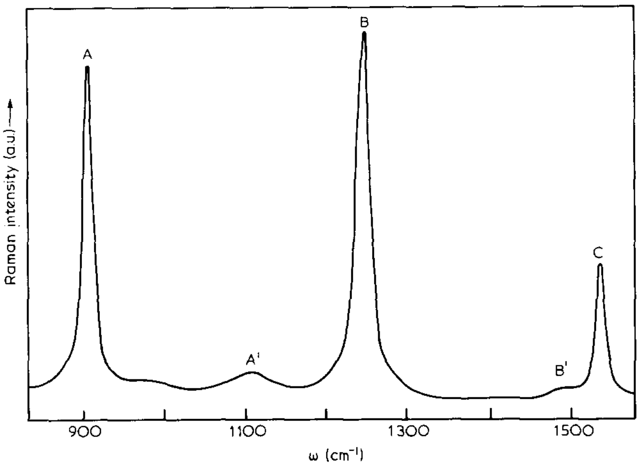

Figure 1 Raman spectra of $(CH)_x$ after polymerization at −78°C; T = 78K; λ_L = 6000 Å. *Cis*-form, lines: A, 908 cm^{-1}; B, 1247 cm^{-1}; C, 1541 cm^{-1}. *Trans*-form, bands: A', 1080–1120 cm^{-1}; B', 1450–1540 cm^{-1}

was limited to 30–40 mW in order to avoid extra isomerization due to local heating.

Figure 1 shows the Raman spectrum of a polyacetylene film polymerized at low temperature (−78°C), after a short period at room temperature necessary to transfer the sample from the Pyrex cell where it was stored at liquid nitrogen temperature to the Raman cryostat. This spectrum reveals a high content of *cis*-form in the film from the intense A,B,C lines, while the A' and B' bands characteristic of the *trans* form are weak. This is in good agreement with Shirakawa's observations[8] and the e.p.r. studies reported recently[4].

Oxygen effects have been studied by comparing two samples taken from the same piece of polyacetylene with characteristics shown in *Figure* 1. Sample 1 was stored under vacuum and sample 2 was stored in air, both under the same temperature conditions. Raman spectra were taken from time to time and those obtained after one month of this treatment are shown in *Figures* 2*a* and 2*b*. *Figure* 2*a* resembles *Figure* 1, which implies that the sample has not changed much at least with respect to the *cis–trans* content. However, *Figure* 2*b* reveals a significantly greater *trans* content in the $(CH)_x$ film. Hence, isomerization occurred during this treatment, and this is clearly an effect of oxygen on the film. This observation confirms the e.p.r. results of Bernier *et al*[4].

The bands associated with the *trans*-$(CH)_x$ have a different shape from that usually observed for this exciting wavelength (600 nm). This is particularly evident in the inset of *Figure* 2*b* where the A' band assigned to the C–C stretching vibration has been magnified. This also appears for the B' band assigned to the C=C stretching vibration, but overlapping with the C line of the *cis* form hides the effect. No maximum is seen at 1080 cm^{-1} but a rather flat peak. The width and shape of the *trans* Raman bands are due to a distribution in the chain lengths and the shorter the chains, the higher the frequency[7]. Therefore, isomerization induced by oxygen leads to a larger number of short *trans* sequences than obtained by the usual thermal isomerization.

Having clarified the above points, we studied the effects of a dopant on the oxidized sample. Dopants like I_2 or AsF_5 increase considerably the electrical conductivity of the material and imply a charge transfer from the electrons of the carbon–carbon double bonds. Oxygen, however is expected to fix the chains by a chemical bonding. If so, it will first occupy some free space between the chains and then reduce the length of conjugated double bond sequences. According to these arguments, the doping efficiency with a usual dopant should be reduced. We have therefore exposed samples 1 and 2 together to iodine vapour. The low frequency range Raman spectra show the presence of the I_3^- and I_5^- species[6,7] in larger concentration for sample 1 (especially for I_5^- ions) than for sample 2. In the high frequency range, the $(CH)_x$ lines and bands are no longer observed for sample 1, while they are for sample 2. This is a qualitative argument indicating that sample 1 carefully handled under vacuum has been saturated with iodine while the oxidized sample has not. In a sample strongly doped with iodine[7], backbone vibrations are not observed. The resonance effects which make these vibrations observable in Raman scattering have disappeared because the product dealt with is completely different from the starting material.

Raman scattering has provided useful information about the effects of oxygen on polyacetylene. The isomerization induced by oxygen is demonstrated to be in good agreement with the e.p.r. line assignment for the *trans*-isomer and related experiments[4]. Furthermore, the *trans* sequences obtained are shorter than those obtained by thermal treatment. This result also agrees with the e.p.r. linewidth (8.8 gauss), the 'motional narrowing' being much reduced in this case. No clear effects of oxidation scattering were detected by Raman for a *trans* sample,

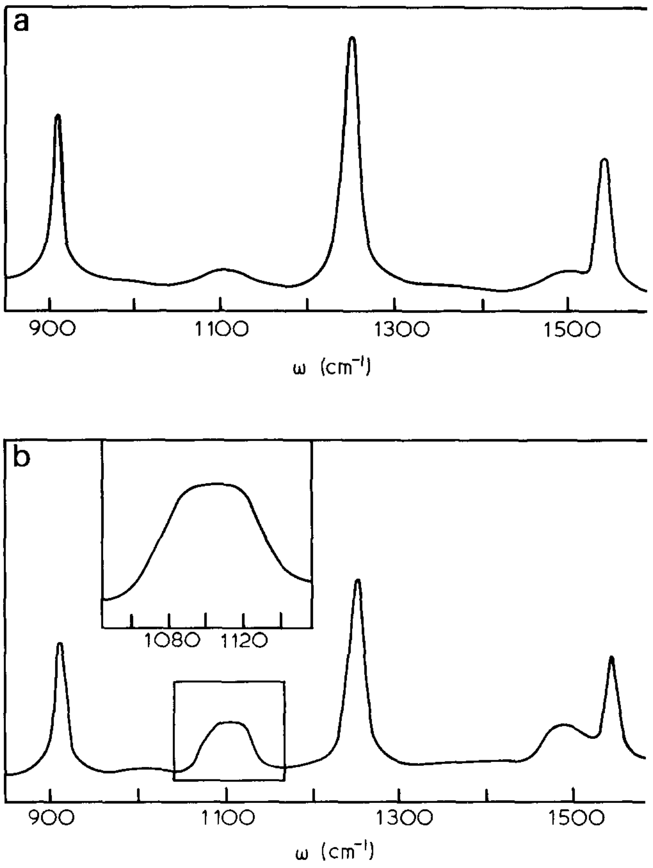

Figure 2 Raman spectra of $(CH)_x$ at T = 78K; λ_L = 6000 Å. (a) Sample 1, after 1 month under vacuum at r.t.; (b) sample 2, after 1 month in air at r.t.

thermally isomerized at 180°C. Therefore, the *trans* sequences, if reduced in length by oxidation, are in large concentration long enough to be considered as infinite with respect to Raman scattering. This result also agrees with the e.p.r. linewidth (2.6 gauss) of an oxidized trans sample.

Finally, the partial incapability of oxidized $(CH)_x$ to be doped has been demonstrated. Oxygen reacts vigorously with the sample and must be excluded to preserve sample properties.

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