

polymer communications

Conductivity measurements during the *cis*-*trans* isomerization of $(\text{CH})_x$ films

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Polyacetylene $(\text{CH})_x$, if synthesized at -78°C as described by Shirakawa *et al.*¹, is almost entirely in the *cis* configuration (Figure 1a), which is unstable at high temperatures. The stable *trans* configuration (Figure 1b) can usually be obtained by different methods: direct polymerization of acetylene at $T > -78^\circ\text{C}$ ²; thermally-induced isomerization of the *cis*-isomer²; or doping of the *cis*-isomer with chemical species such as AsF_5 ³, O_2 ⁴, etc. The cleanest way to obtain a particular *cis/trans* ratio is by thermal treatment of the pure *cis*-isomer prepared at -78°C , which has the largest chains and the smallest number of defects compared with $(\text{CH})_x$ prepared at higher temperatures. Although it is well known² that the resistivity of undoped $(\text{CH})_x$ decreases from $\sim 10^9 \Omega\text{cm}$ for the *cis*-isomer to $10^5 \Omega\text{cm}$ for the *trans*, the isomerization process itself is poorly understood at this time. We describe here conductivity measurements performed during the thermally-induced isomerization of *cis*- $(\text{CH})_x$ films.

The samples were prepared using the procedure of Shirakawa *et al.*¹ at -78°C . Thickness varied from 50 to 200 μm . D.c. conductivity measurements were carried out by the usual four probes techniques, using gold wires fastened with gold paste⁵. Samples were sealed in Pyrex tubes under 300 torr of pure nitrogen in order to ensure a fast thermal treatment of the films when the tubes were immersed in an oil bath at a given temperature T . Measurements were performed for $150^\circ\text{C} < T < 260^\circ\text{C}$ during times up to 24 h.

Results are reported in Figure 2 where the sample resistivity is plotted versus the time t spent at a given temperature. In all cases, we observe that ρ goes through a minimum value ρ_{\min} which decreases with increasing temperature as a consequence of the thermally-activated conductivity behaviour of $(\text{CH})_x$ ^{2,5}. The time t_{\min} at which this resistivity minimum occurs considerably decreases when T increases. We have observed a slight dispersion (no more than 20%) of the ρ_{\min} and t_{\min} values depending on the sample thickness.

Oxidation of the *trans* $(\text{CH})_x$ is known to lead to an increase of the resistivity⁶, which has to be correlated with

a decrease, observed by e.p.r.⁴ for instance, of the effective length of the *trans* sequences due to the creation of defects along the chains. Here, we have verified that the observed behaviour was not due to oxidation of the samples, since measurements were performed under a nitrogen atmosphere as well as under a good vacuum. If not due to the influence of external chemical species, we must assume that the resistivity increase observed for $t > t_{\min}$ is associated with a change of the intrinsic nature of the chains.

Raman studies⁷ have shown that for $t \sim t_{\min}$ the polyacetylene was almost entirely in the *trans* configuration, while an evolution of the *trans* sequence length distribution versus time was observed, the longest *trans* sequences appearing around t_{\min} . The results of Figure 2 strongly suggest that the resistivity minimum is associated with the gradual occurrence of a degradation of the *trans* sequence lengths versus time, appearing for instance as crosslinks between chains or even chain breaking. Consequently at a given temperature we successively observe:

(a) for $t < t_{\min}$, a decrease in resistivity associated with the *cis*→*trans* isomerization;

(b) for $t > t_{\min}$, an increase in resistivity due to the gradual creation of defects along the *trans* chains.

It seems possible to optimize the conductivity of undoped *trans*- $(\text{CH})_x$ by a careful choice of the temperature and duration of the isomerization. Furthermore the electrical properties of iodine-doped samples are also strongly dependent on the conditions of the isomerization process. The Table I presents the resistivities observed for two samples which have been successively isomerized and doped using the following conditions:

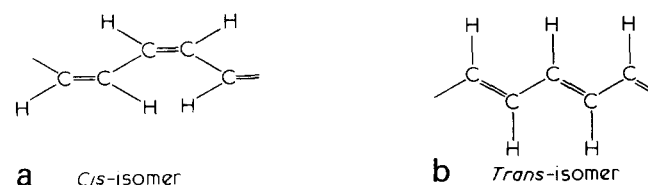


Figure 1 Schematic structure of the two $(\text{CH})_x$ isomers: (a) *cis*-isomer; (b) *trans*-isomer

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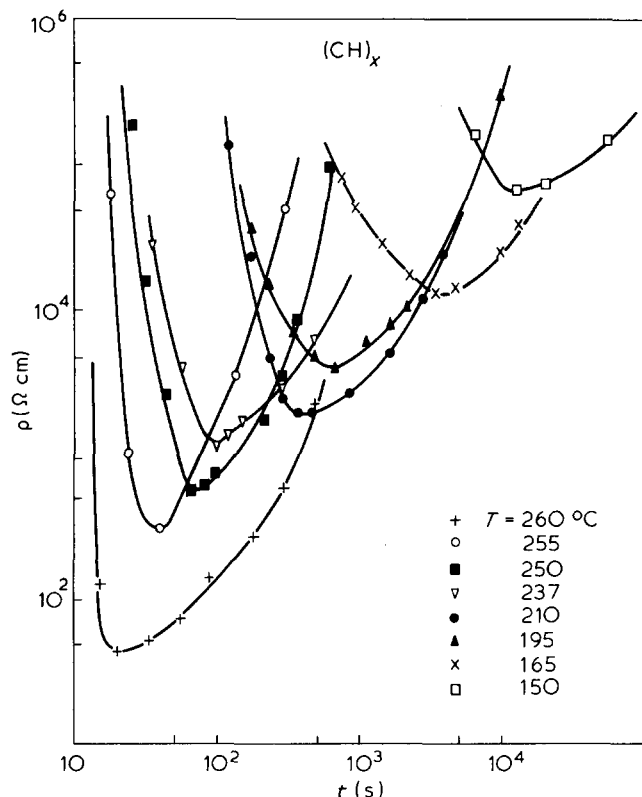


Figure 2 Time dependence of the resistivity of undoped $(CH)_x$ films during the isomerization process at different temperatures between 150° and 260° C. Starting point at $t = 0$ corresponds to almost entirely *cis*- $(CH)_x$ films with $\rho \sim 10^9 \Omega\text{cm}$

Sample 1—isomerized at 200°C for 5 min (corresponding to t_{min} for this temperature), and doped with iodine vapour for 10 h.

Sample 2—isomerized at 200°C for 20 h and doped with iodine vapour for 10h.

From these results it is then clear that:

(i) the resistivity of an iodine doped *trans*- $(CH)_x$ isomerized during the time t_{min} is smaller than any published value⁸;

Stereoselectivity of the ring-opening polymerization of bicyclo[6.1.0]nonene-4

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Ring-opening polymerization of cycloolefins yields high molecular weight polyalkenamers containing double-bonds of both *cis*- and *trans*-configurations. Since the total amount of double bonds present in the system is not changed during the cycloolefin polymerization (the degree of unsaturation of polyalkenamers usually amounting to 100%), the polymer microstructure can be characterized by a single parameter, the proportion of *cis*- units in the polymer (the S value). The investigation of the stereoselectivity of cycloolefin polymerization is, however, often complicated by the fact that the double bonds formed

Table 1

I_2 doped <i>cis</i> - $(CH)_x$	I_2 doped <i>trans</i> - $(CH)_x^*$	Sample 1	Sample 2
$\sim 10^{-2} \Omega\text{cm}$	$\sim 2 \times 10^{-2} \Omega\text{cm}$	$\sim 5 \times 10^{-3} \Omega\text{cm}$	$\sim 1 \Omega\text{cm}$

* *Trans*- $(CH)_x$ used here was obtained in the usual way, i.e. by the isomerization of the *cis*-isomer at 200°C for 1 h

(ii) isomerization performed during times long compared with t_{min} induces so many defects that doping cannot be effective, leading to greater resistivities.

A systematic study of the effects of thermal treatment on undoped and doped $(CH)_x$ is in progress.

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undergo effective isomerization and the polymer microstructure is appreciably changed with conversion¹⁻³.

By extrapolating s to zero conversion an S_0 value can be obtained which is independent of the monomer concentration and the concentration of catalyst components and their ratio but varies with the polymerization temperature. This was previously demonstrated by our studies on cyclooctene (CO) polymerization³.

Using the assumption that one active site can afford two types of structure, *cis* and *trans*, the S_0 value is the stereoselectivity of the elementary process of cycloolefin