Cis–trans isomerization of polyacetylene induced by mechanical rolling

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The influence of mechanical rolling on the e.s.r. spectrum of originally *cis*-rich polyacetylene is investigated. Rolling decreases the peak-to-peak e.s.r. linewidth, ΔH_{pp}. This phenomenon is supposed as being related to *cis-trans* isomerization. However, rolling only slightly increases the *trans* content and the spin susceptibility of the polymer. These observations can be explained by assuming that the rolling induced isomerization preferentially increases the length of the *trans* segments with unpaired spins. Rolling is less effective than heating in giving rise to isomerization within all-*cis* segments or in lengthening *trans* segments with no stable unpaired spins. The behaviour of ΔH_{pp} as a function of *trans* content in the case of rolling induced isomerization is different from the thermally activated process. The e.s.r. linewidth gives information only about the '*trans* macroradicals' and not about the total *cis–trans* isomer ratio, that used to be employed.

Keywords Isomerization; polyacetylene; mechanical rolling; electron spin resonance conformation

Introduction

Polyacetylene (polyvinylene, hereinafter denoted as $(CH)_x$) has recently been the subject of a large number of experimental and theoretical studies[1,2] (and references therein) because of its remarkable electrical, magnetic and other properties. The most unusual property of this polymer is that its electrical conductivity can be varied over 12 orders of magnitude on doping with different donors or acceptors[3].

Polyacetylene consists of a random accumulation of highly crystalline fibres with a diameter in the order of 20 nm[4]. X-ray measurements strongly suggest that the molecular chains are parallel to the fibre axis[5]. The fibres occupy only a fraction of the total volume, therefore the virtual density determined from the mass and dimensions is 1/4–1/2 of the real value, 1.16 g cm^{-3} according to flotation measurements[6].

There exist *cis* and *trans* isomer forms of $(CH)_x$ chains[7–9]. The two possible *cis* skeletons are the *trans-cisoid* and the *cis–transoid*. According to the calculations of Yamabe *et al.*[8] the *trans–cisoid* form is less stable than the *cis–transoid*. The polymerization of acetylene in the presence of a Ziegler-type catalyst primarily yields polymer in the *cis* configuration which can be isomerized into all-*trans* by heating[10,11].

Bond alternation is present in the polymer which thus reduces its energy compared with the uniform chain[12]. During the *cis–trans* isomerization neutral defects are formed in the bond alternation[13]. In these defects the phase of bond alternation changes by 180°. This means that the 'single' and 'double' bonds are shifted by one carbon–carbon distance and one unpaired electron is left behind. These unpaired electrons are responsible for the paramagnetic properties of polyacetylene[14].

It was pointed out by Bernier *et al.* that such defects exist only in the all-*trans* segments[15,16]. The two sides of a *trans* isomer chain separated by this defect have equal energy in a structure unit, hence the spin can be shifted without any change of energy. This is in accordance with the 'motionally narrowed' e.s.r. line observed in this case[14]. On a *cis* backbone a shift in the bond alternation changes the symmetry and hence the energy of the chain. (For example, a *cis–transoid* structure would turn into a *trans–cisoid* structure.) For this reason mobile spins cannot exist in a *cis* segment. The relatively broad e.s.r. signal observed in *cis*-rich samples is attributed to short *trans* segments with an unpaired spin. Thus, the e.s.r. signal in polyacetylene yields information only about the all-*trans* polyenyl radicals.

During heat-induced isomerization, as the *trans* content increases, the spin susceptibly χ_p also increases, while the e.s.r. linewidth decreases[11,13]. This is interpreted as an increase of both the number and mean length of the *trans* segments. Isomerization of a few per cent was also observed after stretching the *cis*-rich samples by mechanical elongation[17]. It was shown by proton n.m.r. measurements that mechanical rolling also caused partial isomerization[18].

In order to make clear the influence of the mechanical rolling on the *trans* polyenyl radical structure we have investigated the e.s.r. spectra and the *cis–trans* composition of originally *cis*-rich polyacetylene films before and after rolling.

Experimental

Polyacetylene films were synthesized by the method developed by Ito *et al.*[4], using a $Ti(O\text{-}n\text{-}Bu)_4\text{-}AlEt_3$ homogeneous catalytic system in toluene. Polymerization was performed at −78°C in order to obtain a *cis*-rich isomer. The samples used in this study were cut from flexible, shiny foils of 20–100 μm thickness.

The isomer content of the samples was determined from their infra-red spectra according to Ito *et al.*[4] using the *trans* C–H and *cis* C–H out-of-plane deformation bands at 1015 cm^{-1} and 740 cm^{-1}, respectively. The *cis* content of polyacetylene was calculated from the formula:

$$cis\ \text{content}\ [\%] = 100[1.30\ A_{cis}/(1.30\ A_{cis} + A_{trans})] \quad (1)$$

where A_{cis} and A_{trans} are the absorbances at the above frequencies.

The absorption i.r. spectra were recorded on a NICOLET 7199 FT i.r. spectrometer. The number of scans was at least 200.

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The A_{cis} values of *cis*-rich polymers were very high. The i.r. spectra could be evaluated when the effective surface density of $(CH)_x$ films was $\sim 1.5 \times 10^{-3}$ g cm^{-2}. This means that unrolled foils 20–25 μm in thickness had to be used. In this case A_{cis} was in the order of 2.5 and the corresponding A_{trans} was ~ 0.3.

Whereas A_{trans} could be measured precisely, the high A_{cis} absorbances may be substantially distorted due to the stray light arising from imperfections of the sample. This may lead to an overestimation of the real *trans* content.

The films had an initial *cis* content of 90–92%. Their bulk density determined from the mass and dimensions was 0.65 ± 0.05 g cm^{-3} and 1.14 ± 0.01 g cm^{-3} as obtained from the flotation measurements which were performed in a density gradient column containing toluene and carbon tetrachloride. The samples were kept under vacuum at dry ice temperature before the measurements were taken.

E.s.r. spectra were investigated using a JEOL-FE3X spectrometer working in the *X*-band. Mn^{++}–MgO powder was utilized as a reference signal and VARIAN standard containing 3.0×10^{15} spins/cm for the spin density measurements. All measurements were carried out at room temperature and *in vacuo* of better than 1 torr.

The as-prepared $(CH)_x$ films were rolled using an electric rolling device with controlled gap between its two chrome-covered cylinders. The gap was decreased in 10 μm steps and the samples were rolled several times. This procedure was carried out in the atmosphere at room temperature. The mean thickness before (d_o) and after (d_i) rolling was determined from at least 15 measured data values. We used the reduced thickness (d_i/d_o [%]) to characterize the thinning.

The samples were exposed uniformly to air for 15–20 min, and then placed in e.s.r. tubes and evacuated.

Results

In *Figure 1* the bulk density of the samples is plotted as a function of the reduced thickness, d_i/d_o. After thinning the polymer films to a $(d_i/d_o)_l$ of $\sim 50\%$, their bulk density reaches the fibre density (1.14 g cm^{-3}). Up to this point the pores between the $(CH)_x$ fibres vanish due to the rolling. Near this $(d_i/d_o)_l$ value the films become compact and hard. As expected, the fibre density from flotation measurements remains constant during the rolling.

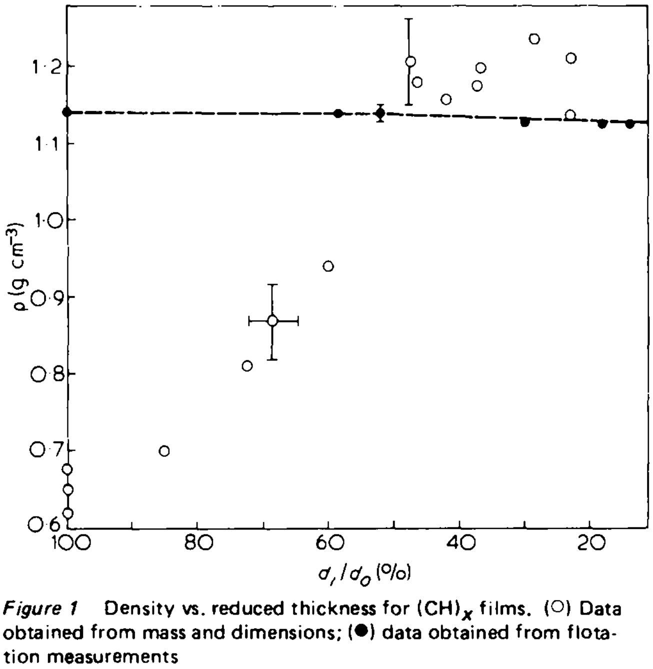

Figure 1 Density vs. reduced thickness for $(CH)_x$ films. (○) Data obtained from mass and dimensions; (●) data obtained from flotation measurements

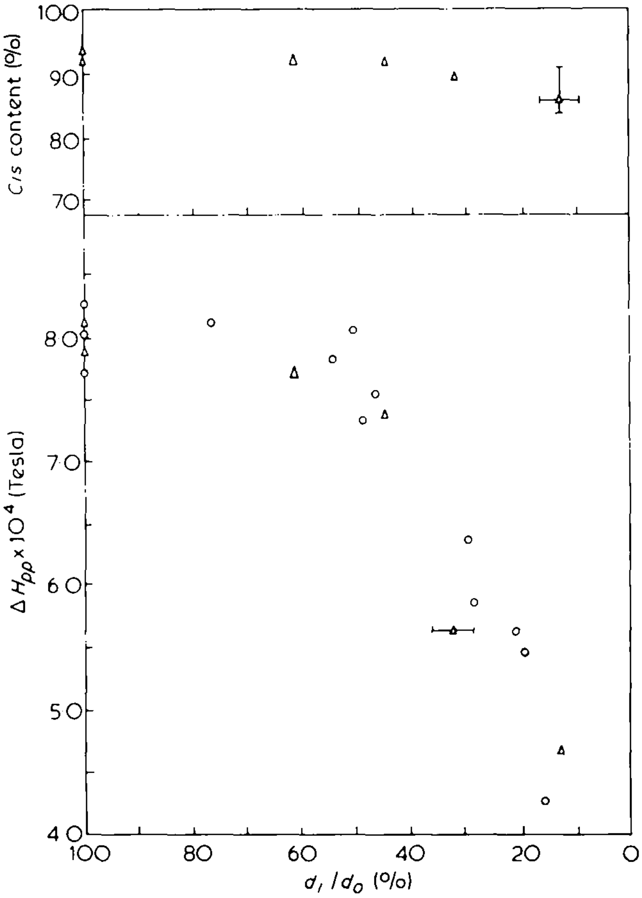

Figure 2 E.s.r. peak-to-peak linewidth and *cis* content as a function of reduced thickness. Isomer content was measured on samples marked (Δ)

The e.s.r. peak-to-peak linewidths and the *cis*–*trans* composition obtained from the i.r. spectra are shown in *Figure 2* as a function of reduced thickness, d_i/d_o. E.s.r. measurements were also performed on the same batch of samples on which the i.r. spectra were recorded. The e.s.r. linewidths of these samples are marked in *Figure 2*. As can be seen from this figure, ΔH_{pp} remains constant until the bulk density of $(CH)_x$ reaches the density of the fibres. As the samples are thinned further, ΔH_{pp} begins to decrease.

Shirakawa and coworkers reported e.s.r. linewidth data as a function of the *trans* content of $(CH)_x$[11]. For the experiments they used polymers obtained by thermal *cis*–*trans* isomerization of a *cis*-rich $(CH)_x$. According to their data the decrease in ΔH_{pp} is connected with an increase in the *trans* content. Shirakawa's results are plotted in *Figure 3* together with our data. It can be seen that in rolled samples ΔH_{pp} rapidly decreases as a function of the *trans* content in contrast to thermal isomerization. The *trans* content of the rolled sample with a linewidth of 4.7×10^{-4} Tesla (4.7 Gauss) was found to be less than 14% whereas in the case of the heated samples of Shirakawa, a *trans* content of 32–46% corresponds to this linewidth.

The initial ΔH_{pp} of *cis*-rich samples is obviously a function of preparation. As mentioned above, the ΔH_{pp} of *cis*-rich samples is determined by the mean conjugation length of *trans* polyenyl radicals. Thus the discrepancy in the magnitude of ΔH_{pp} between our data and Shirakawa's data is a question here of minor importance, and it is

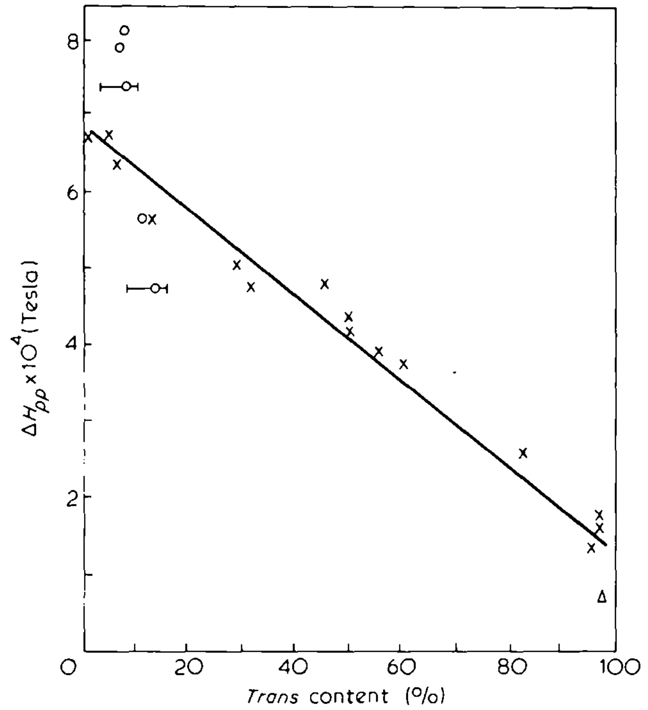

Figure 3 E.s.r. peak-to-peak linewidth vs. *trans* content: (X) data from ref. 11 measured in heat treated samples; (O) our data measured in rolled samples; (Δ) our results obtained in a sample completely isomerized by heating

probably due to the difference in the conjugation length of 'macroradicals' in the initial samples.

Exposure of $(CH)_x$ to air increases the ΔH_{pp} of both the *cis*[19] and the all-*trans*[20] isomers. The e.s.r. linewidths of the rolled samples after a 30 min heat treatment at 180°C decreased to 7×10^{-5} Tesla (0.7 Gauss). This residual linewidth is rather small and shows that the exposure of the samples to air for a short period has only a minor influence on the results.

The spin susceptibility χ_p of the samples was also measured as a function of d_i/d_0. The results are shown in *Figure 4*. The spin susceptibility as a function of thinning remains constant within the experimental error of ±15%.

Discussion

We focus on the explanation of the observed rapid decrease in ΔH_{pp} following the thinning of $(CH)_x$ whereas only a slight increase in the *trans* content and in χ_p was observed.

It was mentioned that the unpaired electrons in $(CH)_x$ are related to *trans* segments. The magnitude of ΔH_{pp} of *cis*-rich polymer is determined by the mean delocalization length of the spin[21] (i.e., by the mean length of *trans* segments with unpaired electrons). Thus any change in ΔH_{pp} should above all indicate a change in the mean conjugation length of polyenyl radicals. The conjugation length *n* of polyenyl 'macroradicals' (the number of $-CH=CH-$ units) and ΔH_{pp} are related[21]:

$$\Delta H_{pp}\propto n^{-1/2} \qquad (2)$$

This relationship should be approximately valid if ΔH_{pp} is controlled by the unresolved hyperfine structure of fixed spins and surrounding protons. It may be supposed that in *cis*-rich $(CH)_x$ the *trans* segments are not long enough to allow spin diffusion since delocalization of the defects is expected to extend to several CH units[14,22]. Therefore, in such a case, a motionally narrowed e.s.r. line cannot form. This assumption is also supported by dynamic nuclear polarization measurements[23].

We explain the observed decrease in e.s.r. linewidth by the extension of the length of *trans* segments with unpaired spins. Using relationship (2) a decrease in ΔH_{pp} from 8×10^{-4} Tesla to 5.5×10^{-4} Tesla would indicate a twofold increase in the mean length of *trans* polyenyl 'macroradicals'. The initial spin concentration is of the order of 5×10^{-5} spins/CH unit and the corresponding mean radical length using Ohnishi's results[21] was estimated to be near 20 $(CH)_2$ units. An increase of the length of radical segments by a factor of 2 in itself gives rise to a negligible increase of the trans content. The lack of variation of χ_s together with the small increase of the *trans* component shows that relatively few 'new' *trans* segments are formed. This may be contrasted with the isomerization by heat treatment investigated by Shirakawa *et al.*[11] (see *Figure 3*). For isomerization by heat treatment the linewidth decreases less rapidly with *trans* content and there is a substantial increase in χ_p also[11,13]. Thus for this case also 'new' *trans* segments are initiated.

The growth of the polyenyl radicals during the rolling begins when the films are thinned below d_i/d_0 of ~50% (i.e. when the pores between the $(CH)_x$ fibres are removed). On further thinning, the length of the samples along the direction of the rolling increases. Parallel with the lengthening of $(CH)_x$ films there is a possibility that the fibres become aligned and the chain segments become ordered *via* bond rotation.

Cis–trans isomerization takes place in the presence of unpaired spins on the rotating bonds[13,14]. The *cis–trans* 'border' can thus shift thereby decreasing the *cis* part of the chain in the presence of an unpaired spin with a small energy compared with a 'border' with no unpaired spins.

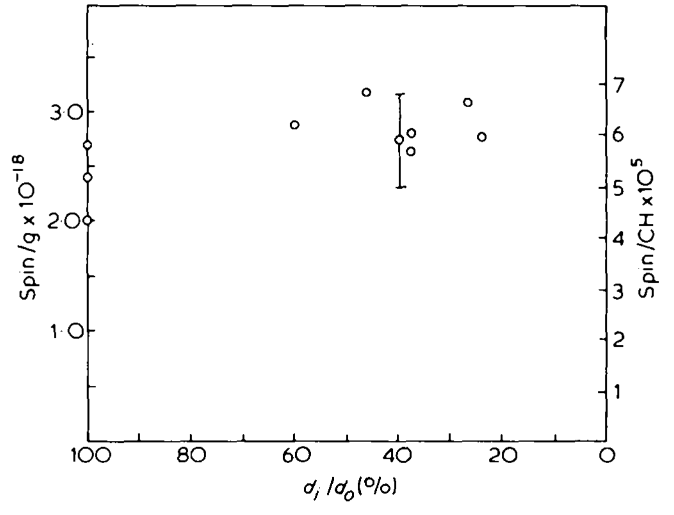

Figure 4 Spin density vs. reduced thickness

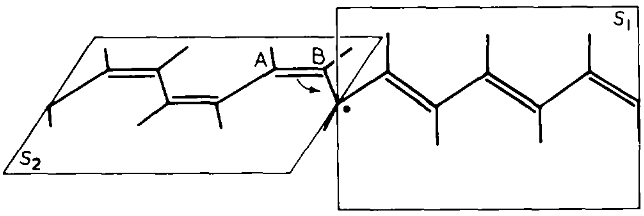

Figure 5 Idealized, schematic illustration of proposed mechanism of *cis–trans* isomerization. The plane of the *cis* segment, S_2 is perpendicular to that of the trans, S_1. In the next step of isomerization due to the marked bond rehybridization, the unpaired electron shifts to the C atom labelled A and the C atom labelled B transfers to plane S_1

In this case the isomerization is related to a rotation of C–C single bonds[24]. The phenomenon is illustrated in *Figure 5*. Rolling maintains the spin concentration but extends the length of the *trans* radicals and thus slightly isomerizes polyacetylene. The observed spins were presumably formed by the heat induced isomerization which took place when the temperature first rose from −78°C to room temperature.

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Electrical conduction in Kapton polyimide film at high electrical fields

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Electrical conduction in Kapton polyimide film was studied under steady-state conditions in the temperature range 100°–200°C and in electric fields of 50–450 kV cm^{-1}. An attempt was made to fit the field dependence of current to one of the several possible mechanisms which have been proposed by different workers. Evidence is presented to suggest that even at high fields ionic conduction may be the operative mechanism of conduction. Values of ionic jump distance of 50–60 Å show good agreement with values reported by other workers.

Keywords Electrical properties; conduction; Kapton polyimide; film; mechanism; ionic jump

Introduction

Kapton, whose chemical name is poly(4,4′-diphenylene pyromellitimide) is a film forming polymer manufactured by EI du Pont de Nemours and Co. Inc., USA. It is known to be strongly heat resistant, is little affected by various kinds of chemicals and has excellent electrical properties as an insulator. It is ideal for use as an insulator under adverse environmental conditions such as those encountered in outer space. However, Kapton is photoconductive[1] which also arouses interest of another kind—its possible use as a photoreceptor in electrophotographic and energy conversion applications. In order to exploit this potential it is essential to understand the mechanism of electrical conduction in the material.

Several workers have reported the results of their investigations in this field. But there is no reasonable agreement among them on the type of conduction mechanism in Kapton, especially at high electric fields. At

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