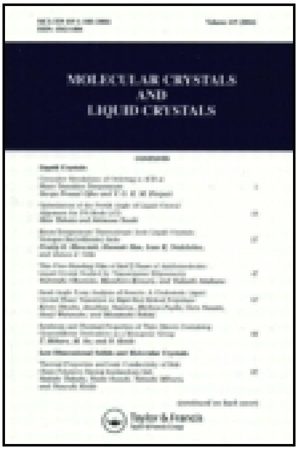

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NARROWING MECHANISMS OF ESR LINE OF $(CH)_x$

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Electron Spin Resonance (ESR) on the paramagnetic centers in undoped polyacetylene $(CH)_x$ was studied and the effects of the thermal isomerization and the oxidation on the narrowing mechanisms of an ESR line were discussed. The ESR linewidth at 4.2 K is found to be proportional to $n^{-1/3}$ (n: spin density in $(CH)_x$) which means that the static narrowing mechanism was three-dimensional exchange narrowing. The linewidth at room temperature changed with the thermal isomerization and oxidation of $(CH)_x$ and was explained by two opposed mechanisms; motion of spins in the conjugated chain and restriction of the motion by cutting off the conjugated chain by cis content or oxidation.

INTRODUCTION

Polyacetylene $(CH)_x$ is the one-dimensional organic conductor having cis and trans isomers. By the thermal isomerization cis-$(CH)_x$ is transformed to trans-$(CH)_x$. During the cis/trans isomerization magnetic defects, so called neutral solitons, are created.[1,2] The properties of a neutral soliton were studied earlier by X-band ESR experiment of undoped $(CH)_x$ with emphasis on the temperature dependences of the linewidth (Fig. 1).[3] Using Anderson-Weiss's formula[4] for narrowed linewidth, results were analysed in terms of one kind of spins to show the co-operative contribution from two narrowing mechanisms; temperature dependent and temperature independent mechanisms.[3]

To explain the effect of the oxidation on the ESR linewidth at room temperature, a "two kinds of spin" model was proposed.[5] This model considered two kinds of spins as the ESR center; a localized spin around the oxygen and a diffusive spin on the polymer chain, and explained the broadening of the ESR linewidth with oxidation.

In this paper we present the spin density dependence (with the thermal isomarization and the oxidation) of the ESR linewidth of the undoped polyacetylene at 4.2 K and room temperature and discuss the narrowing mechanism.

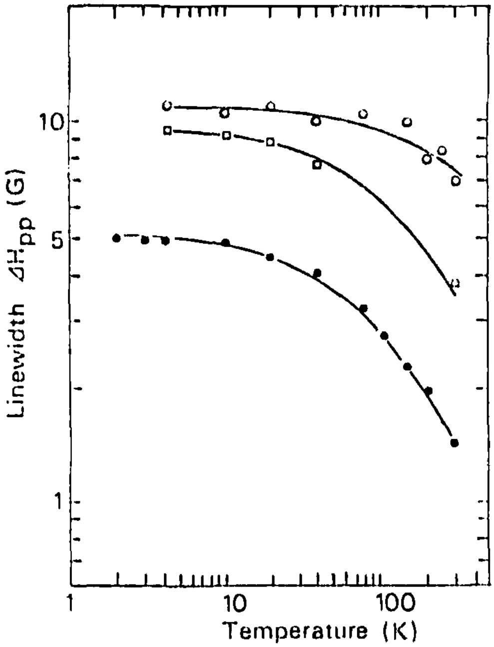

FIGURE 1 Temperature dependence of peak to peak linewidth of the first derivative of the ESR absorption line of undoped polyacetylene: ○ cis- ; ▫ 50 % cis/trans- ; ● trans-$(CH)_x$.

SAMPLE TREATMENT

Polyacetylene films were synthesized using the techniques developed by Ito, Shirakawa, and Ikeda.[6]

Thermal Isomerization

An undoped cis-rich-$(CH)_x$ film was sealed in vacuum in a quartz tube and heated in an oil-bath at 110 °C, 135 °C, and 145 °C for 20 minutes, respectively. The spin density was decided by the double integrated intensity of the first derivative of the ESR absorption line, which was compared with the intensity of the standard sample, DPPH, at room temperature.

The variation of the relative spin density with the isomerizing temperature is shown in Fig. 2. The spin density increases as the isomerization proceeds as shown earlier.[7] The line shape deviates from Lorentzian ($\Delta H_{1/2}/\Delta H_{pp} \simeq 1.3$) in cis-rich-$(CH)_x$ and becomes nearly Lorentzian in $(CH)_x$ isomerized at 145 °C for 20 minutes.

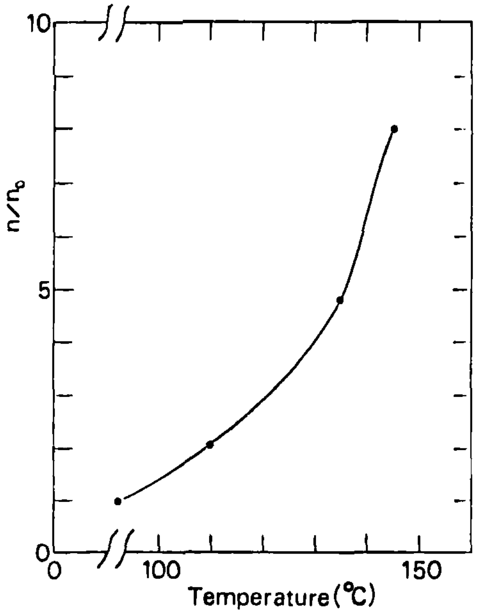

FIGURE 2 The increase of the spin density of undoped $(CH)_x$ by thermal isomerization. The sample was heated twenty minutes at each temperature.

Oxidation

An undoped trans-$(CH)_x$ (thermally isomerized at 192 °C for an hour) was in an H_{104} microwave cavity which was evacuated and filled with pure oxygen (1 atm). The variation of the relative spin density with the oxidation time is shown in Fig. 3. As shown in the figure the spin density increases in an earlier stage of the oxidation and then decreases. These facts suggests that the oxidation of $(CH)_x$ consists of two different processes; fast charge transfer reaction process and slow oxygen addition reaction process. The fast process increases the elctron density and the slow process decreases the electron density in $(CH)_x$.

NARROWING MECHANISMS OF ESR LINEWIDTH

Figure 4 shows the spin density dependence of $\Delta H_{1/2}$ (full width at half power of the ESR absorption line) as the thermal isomerization advances.

Figure 5 shows also the spin density dependence of $\Delta H_{1/2}$ with the oxidation.

Static Narrowing Mechanism

The spin density of undoped $(CH)_x$ increases with the thermal isomerization and the ESR line becomes narrower. The linewidth at 4.2 K in Fig. 4 is nearly proportional to $n^{-1/3}$,

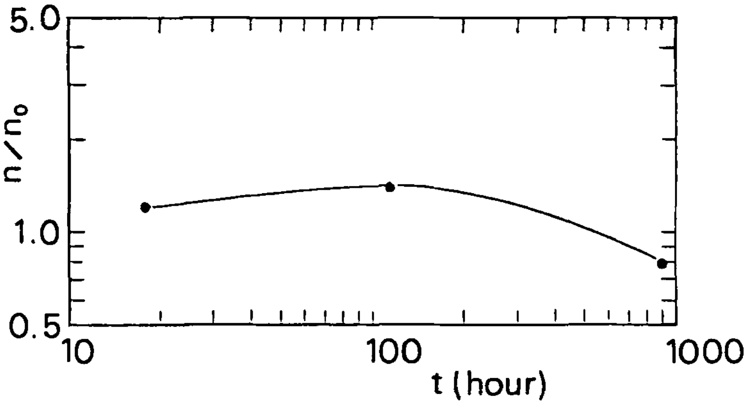

FIGURE 3 The variation of the spin density of undoped $(CH)_x$ vs. oxidation time. The sample was sealed with pure oxygen (1 atm).

where n is the spin density of the polyacetylene films used.

Figure 5 also shows $n^{-1/3}$ dependence of the linewidth at 4.2 K, which is the same n dependence as the thermal isomerization process (Fig. 4).

These facts mean that the linewidth at 4.2 K is proportional to the inverse of the mean distance between spins in three dimensional space and independent on the method of increasing the spin density. Considering that the line shape of trans-$(CH)_x$ is Lorentzian even at 4.2 K where the motional narrowing is ineffective, and that $\Delta H_{1/2}$ is proportional to $n^{-1/3}$, the temperature independent narrowing mechanism will be three-dimensional exchange narrowing.

Motional Narrowing Mechanism

As shown in Fig. 1, the ESR linewidth of undoped $(CH)_x$ becomes narrower with temperature, that is, the thermal motion of the unpaired spin dominates the narrowing mechanism of the linewidth around the room temperature. We have suggested that some diffusive motion rather than the classical thermal motion of solitons needs to explain the

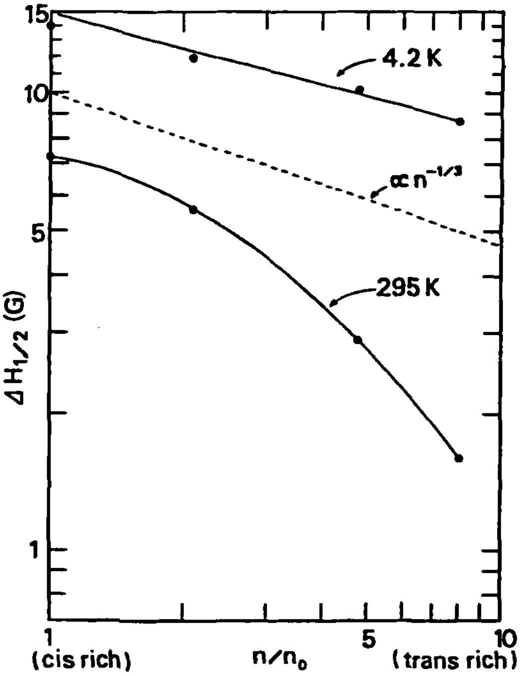

FIGURE 4 The spin density dependence of the ESR full-width at half power by the thermal isomerization process.

motional narrowing.[3]

The spin density dependences of the ESR linewidth of undoped polyacetylene at room temperature are shown in Fig. 4 (thermal isomerization process) and in Fig. 5 (oxidation process). (Note that the oxidation time advances with the number written around the experimental point.)

In Fig. 4 the linewidth at room temperature becomes narrower with the spin density. This narrowing process can be understood with the consideration that, in addition to the static narrowing mechanism, the motional narrowing mechanism becomes effective in trans-rich-$(CH)_x$ which has longer conjugated chains than cis-rich$(CH)_x$.

On the other hand the room temperature linewidth of oxidized trans-$(CH)_x$ becomes wider though the spin density becomes larger (that is, the exchange narrowing mechanism comes to effective) in the fast oxidation stage. This fact seems to reflect the modification of the conjugated chain by the oxidation which restricts the motion of the spins, and the motional narrowing mechanism is weakened.

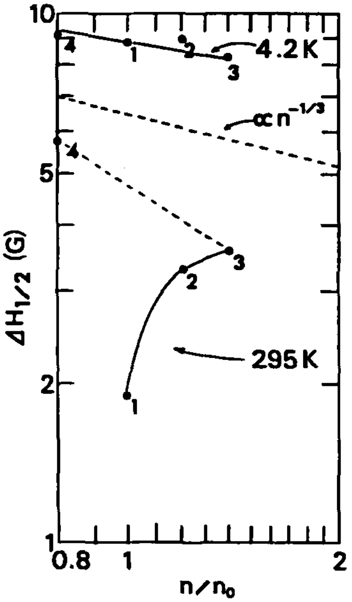

FIGURE 5 The spin density dependence of the ESR full-width at half power by the oxidation process. The oxidation time advances with the number written around the experimental point.

SUMMARY

The temperature dependence, the thermal isomerization dependence and the oxidation dependence of the ESR linewidth of the undoped polyacetylene can be explained by the three-dimensional exchange narrowing and the motional narrowing mechanisms. Only one kind of spins (neutral solitons) in the conjugated chain is considered to contribute to these mechanisms.

On the other hand, Holczer et al. proposed the "two kinds of spin" model to analyze the oxidation dependence of the ESR linewidth at room temperature.[5] They assumed the two kinds of spins; the diffusive spins in the polymer chain and the localized spins around the oxygen. They showed the observed linewidth at room temperature is given as,

$$\Delta H = C\Delta H_L + (1-C)\Delta H_D, \qquad (1)$$

where C is the relative concentration of the localized spins, and ΔH_L and ΔH_D are the linewidths of the localized and diffusive spins respectively.

The oxidation dependence of the linewidth at 4.2 K can be explained by the "two kinds of spins" model as follows. If the motion of the diffusive spin becomes slower and ΔH_D approaches to ΔH_L at lower temperature, eq. (1) becomes $\Delta H = \Delta H_D$ $(= \Delta H_L)$. Thus "two kinds of spins" model coincides with "one kind of spins" model. Then the spin density dependence of the linewidth at 4.2 K can be explained when ΔH_D is proportional to $n^{-1/3}$. Further experiment on the temperature dependence of the linewidth at various oxidation stages will be helpful to see the dynamics of the spins in $(CH)_x$.

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