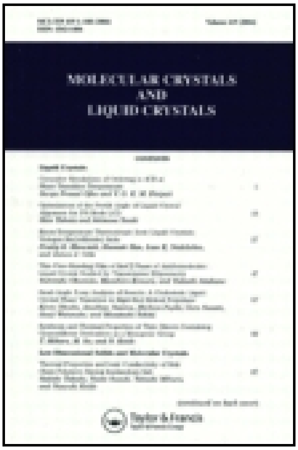

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Remnant Cis Bonds in "Trans"-Polyacetylene

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REMNANT *CIS* BONDS IN "*TRANS*"-POLYACETYLENE

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Abstract We report the infrared spectra of "*trans*"-polyacetylene that has been thermally prepared from *cis*-$(CH)_x$. The minimum of 5-7 percent residual 740 cm^{-1} absorption observed for all cases studied is suggested to be due to isolated remnant *cis* linkages. It is shown that these remnant *cis* linkages may confine the neutral soliton and hence affect the neutral soliton diffusion coefficient. Implications for the soliton generation mechanisms and for conjugation lengths derived from Raman spectra are pointed out.

I. INTRODUCTION

Trans-polyacetylene has been the subject of intense scrutiny, yet controversy remains. In our study of the *cis* to *trans* isomerization[1], we have shown that there is always residual 740 cm^{-1} absorption which comprises ~ 5% of the sample when analyzed as a *cis* double bond. The presence of these *cis* linkages has implications for understanding the creation of solitons and their diffusion as well as determination of *trans*-conjugation lengths from Raman spectroscopy.

II. EXPERIMENTAL TECHNIQUES

Cis-polyacetylene was prepared in situ on 25 mm KBr discs using the normal Shirakawa catalyst composition and concentration.[2] Films were < 10 μm thick, comprised of 500 Å fibrils and were highly crystalline. Thermal isomerization was carried out in situ under argon in a Digilab FTIR (1 cm^{-1} resolution). Isomeric compositions were determined from the ratio of the integrated intensities of the *cis* and *trans* absorptions at 740 and 1010 cm^{-1}, respectively.[1]

III. RESULTS AND DISCUSSION

Figure 1 shows the evolution of the spectra for a typical isothermal isomerization at 100°C; note the residual 740 cm^{-1} absorption which was present even after isomerization for 552 hours. Similar results were obtained for isomerization at 180°C. In no case have we ever observed complete removal of the 740 cm^{-1} absorption.

A. Nature of the Remnant Cis Linkage

Figure 2 illustrates the *trans* chain sequence in the presence of isolated *cis* linkages. The remnant *cis* segments may be in either the *cis-transoid* or *trans-cisoid* configuration. Both forms are expected to display C-H out-of-plane vibrations at ~740 cm^{-1} and are therefore indistinguishable on that basis.[3] The *trans-cisoid* form is assumed to be the lower energy configuration because of the larger strain imposed on the *cis-transoid* form (which in the unconstrained state would have a bend in the chain) by the crystal structure. Note that the phase of the dimerization reverses upon going through the remnant *cis* linkages, in accord with the scrambling of the bond order found in *trans*-polyacetylene by nutation NMR.[4]

B. Soliton Generation

The remnant *cis* linkages within the *trans* crystal structure experience considerable strain. At high enough temperature, the central double bond of the *cis-transoid* configuration may open to form the diradical, followed by electronic rearrangement to the *trans-cisoid* form in which the strain is more readily accommodated by a distortion of the central single bond. The

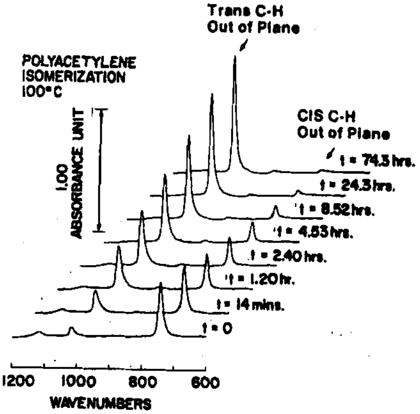

FIGURE 1. Evolution of IR spectrum of $(CH)_x$ during isomerization.

individual radicals so formed may then diffuse away to form two isolated neutral solitons. Cleavage of additional *cis-transoid* double bonds on the same chain would lead to little further increase in soliton population, because of annihilation of soliton-antisoliton pairs. This mechanism would result in the formation of ~two neutral solitons per polyacetylene chain, in agreement with experiment.[5] The bond breaking process is expected to be thermally activated. At low annealing temperatures each remnant *cis* site may be considered independent. Using a two energy level scheme with energy separation, δ, then the number of neutral solitons created, N_S, is related to the number of remnant *cis* linkages, N_C, by

$$N_S = 2N_C \exp(-\delta/k_B T_a) \qquad (1)$$

where T_a is the highest annealing temperature.[6] For concentrations of more than two remnant *cis* linkages per chain, the equation over-estimates the number of solitons because it does not take into account annihilation of soliton pairs. Available experimental data[7] are in accord with this picture.

C. Soliton Motion

In Fig. 2a, a neutral soliton is shown schematically on the left hand side of the *cis* link. In Fig. 2b, the soliton is shown having moved to the right. This causes a reversal of the bonds at the *cis* linkage, forming a *cis-transoid* configuration, which is higher in energy than the *trans- cisoid* by an amount ΔE. The presence of a remnant *cis* linkage in its low energy state then presents a barrier to soliton motion.

The intrachain diffusion rate may then be approximated as the product of the microscopic diffusion rate for an uninterrupted *trans* segment (D_0) times the probability of the soliton having sufficient energy to reverse n *trans-cisoid* linkages in an average chain:

$$D \sim D_0 \, [\exp(-\Delta E/k_B T)]^n \qquad (2)$$

Though ΔE is not known exactly, assuming $\Delta E = 0.01$ eV, a chain length of 500 double bonds[8] and 6% remnant *cis* half of which are *trans-cisoid*, $n = 15$ and $D \sim D_0 \, [\exp(-0.01 \text{ eV}/k_B T)]^{15} = D_0 \exp(-0.15 \text{ eV}/k_B T)$. As seen by Eq. 2, the probability of a soliton visiting a distant part of a chain falls off rapidly due to the cumulative effect of many small barriers. This is in agreement with a distribution of "trapping energies,"[9] although the trap is no longer associated

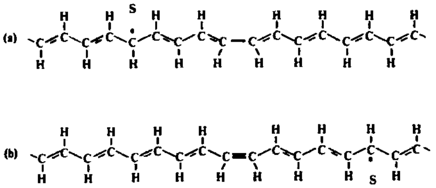

FIGURE 2. Reversal of remnant *cis* dimerization phase with soliton motion.
(a) Remnant *cis* in *trans-cisoid* configuration with soliton on left.
(b) Remnant *cis* in *cis-transoid* configuration with soliton on right.

with oxygen contamination,[9] but rather with remnant *cis* linkages. As readily seen from Eq. 2, at some low temperature, the probability of reaching distant parts of the chain becomes very small, so that nuclear spin diffusion to weakly confined solitons will dominate at low temperatures.[10]

On the basis of nutation NMR spectroscopy[4] and a study of the nuclear spin lattice relaxation rates, it was proposed[11] that only ~3% of the *trans* chains contained solitons, that spins on these chains are rapidly relaxed by moving solitons, and the rest more slowly by nuclear spin diffusion. This ~3% may represent only the *trans* chain segments between two remnant *cis*-linkages that contain a soliton. Hence, the soliton may slowly diffuse through the *cis* link barrier only to be localized in the neighboring region for a relatively long time. Then the soliton may visit the entire chain but in a time scale too slow for NMR technique to measure.

D. Raman Spectroscopic Implications

There have been extensive studies of the Raman band profiles for "*trans*"-$(CH)_x$.[12] The asymmetric peak profiles have been well fit by a bimodal distribution of chain lengths.[12] It is suggested here that the remnant *cis* linkages may act to give effective short chains in Raman spectroscopy (number of trans C = C units between remnant *cis* linkages).

REFERENCES

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1. H.W. Gibson, et. al., J. Phys. (Paris) C3-44 123 (1983); H.W. Gibson, et. al., Amer. Chem. Soc. Polym. Preprints 24 (2), 153 (1983).
2. T. Ito, H. Shirakawa, and S. Ikeda, J. Polym. Sci., Polym. Chem. Ed. 12, 11 (1974); 13, 1942 (1975). Exposure time of catalyst (0.23 M Ti, 0.92 M Al) to acetylene gas was limited to control film thickness.
3. H. Shirakawa and S. Ikeda, Polym. J. 2, 231 (1971).
4. C.S. Yannoni and T.C. Clarke, Phys. Rev. Lett. 51, 1191 (1983).
5. A.J. Epstein, et. al., Solid State Commun. 38, 683 (1981).
6. A similar model has been proposed for thermal generation of structural defects in chalcogenides: M. Abkowitz and J.M. Markovics, Phil. Mag. B 49, L31 (1984).
7. P. Bernier, et. al., J. Phys. Lett. (Paris) 42, L295 (1981); H. Kuzmany, et. al., Mol. Cryst. Liq. Cryst. 77, 197 (1981); A. Zanobi and L. D'Ilario, J. Phys. (Paris) C3-44, 309 (1983).
8. J.C.W. Chien, et. al., J. Polym. Sci.: Polym. Lett. Ed. 21, 93 (1983).
9. M. Nechtschein, et. al., Phys. Rev. B 27, 61 (1983).
10. P.E. Sokol, et. al., J. Phys. (Paris) C3-44, 349 (1983); and, Synth. Metals, in press; W.G. Clark, et. al., and M. Maxfield, J. Phys. (Paris) C3-44, 239 (1983).
11. J.C. Scott and T.C. Clarke, J. Phys. (Paris) C3-44, 365 (1983).
12. L.S. Lichtmann, et. al., Chem. Scripta 17, 149 (1981); L. Piseri, et. al., Proc. Eighth Int. Conf. on Raman Spectroscopy, Bordeaux, France, p. 581 (1982); S. Lefrant, et. al., Polym. Comm. 24, 361 (1983); H. Kuzmany, Phys. Stat. Sol. (b) 97, 521 (1980); J. Phys. (Paris) C3-44, 255 (1983).