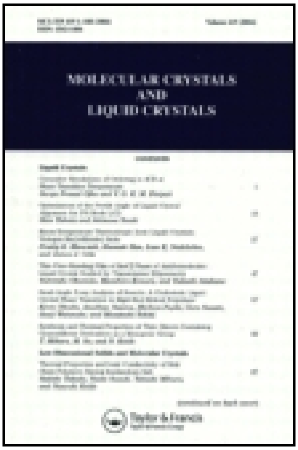

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Isomerization and Spin Generation in Polyacetylene

H. Kuzmany [a], E. A. Imhoff [a], D. B. Fitchen [a] & A. Sarhangi [a]

[a] Department of Physics, Cornell University, Ithaca, New York, 14853, USA

To cite this article: H. Kuzmany, E. A. Imhoff, D. B. Fitchen & A. Sarhangi (1981): Isomerization and Spin Generation in Polyacetylene, Molecular Crystals and Liquid Crystals, 77:1-4, 197-207

To link to this article: http://dx.doi.org/10.1080/00268948108075241

Mol. Cryst. Liq. Cryst., 1981, Vol. 77, pp. 197–207
0026-8941/81/7701-0197$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

ISOMERIZATION AND SPIN GENERATION IN POLYACETYLENE

H. Kuzmany*, E. A. Imhoff, D. B. Fitchen and
A. Sarhangi
Department of Physics, Cornell University,
Ithaca, New York
14853, USA

Received for publication October 8, 1981

The isomerization of undoped $(CH)_x$ was investigated in a combined Raman and ESR experiment. We find that the ESR linewidth, but not the spin concentration, is correlated with the degree of isomerization as determined from the Raman intensities. The spin concentration does not change until the isomerization is well advanced. Hence the decrease in linewidth must be due to the increased mobility of the spins (solitons) rather than exchange interaction. The spin generation is suggested to be due to Diels-Alder crosslinking. The Raman intensities indicate that there are two isomerization processes, with activation energies of 16 and 28 kcal/mole. Anomalous Raman scattering by cis $(CH)_x$ excited with deep red laser light provides additional evidence for defect structures.

CIS-TRANS ISOMERIZATION AND STRUCTURE OF $(CH)_x$

Polyacetylene $(CH)_x$ has attracted very strong interest in chemical and physical research work recently. This is mainly due to the very strong enhancement of conductivity upon doping[1], an unusually strong and narrow ESR line coupled with well expressed Overhauser effect in ENDOR

---

*On leave from the University of Vienna and the Ludwig Boltzmann Institute in Vienna.

experiments[2,3] and a very strong and unusual resonance Raman effect.[4-6] According to the current interpretation the magnetic properties are determined by highly mobile spin-carrying domain walls separating the two degenerate ground states of the trans polymer. According to Su, Schrieffer and Heeger[7] these domain walls can be described in a soliton model. The unusual resonance Raman effect in the trans polymer is understood as being due to a distribution of undisturbed conjugations of various length along the chains of the polymer.

Though it is well known that the unusual properties in $(CH)_x$ are induced by the isomerization of the polymer from cis to trans, little effort has been put on a better understanding of this isomerization process. One reason for it might be that isomerization in a solid at temperatures as low as 100 C is difficult to understand in general because of the strong steric hindrance of any large scale movements. On the other hand it was shown by several authors that most of the spins showing the unusual resonance behavior are generated during the isomerization process[2,8].

In this paper we discuss a model describing the process of isomerization and spin generation. Experimental results from a combined ESR and Raman study are used to check on evidence for this model.

In a previous work[9] it was suggested that the isomerization process occurs by a rotation of two adjacent carbons around the chain axis as shown in Figure 1a. This process requires the generation of radicals in order to allow a rotation of the double bond. Since this type of isomerization process is known from finite unsaturated hydrocarbons like cis-butene to require 63 kcal/mole[10], defects along the chain must play an essential role at least for the initiation of the isomerization. Also isomerization can only occur between two defects since the mismatch between a cis and a trans segment on a chain implies an unstable state of increased energy. These defects do not necessarily interupt the conjugation and may thus appear transparent to a soliton. Some defects of the relevant form have been discussed recently by Vanderbilt and Mele[11].

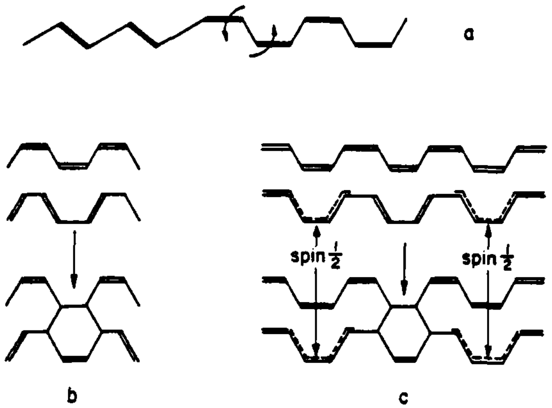

Figure 1. Mechanism for isomerization (a) and spin generation by Diels-Alder cross linking (b) and (c).

In order to explain spin generation during isomerization recall that in finite polyenes Diels-Alder cross linking is frequently observed.[12,13] This process is shown in Figure 1b. It can only happen if a segment with a diene and a dienophile structure (a cis-transoid and a trans-cisoid structure) are facing each other. Since as-polymerized $(CH)_x$ is generally assumed to be all cis-transoid,[13,14] the required trans-cisoid configuration needs to be induced thermally or by isomerization-induced strains. The created section of trans-cisoid is then terminated by two radicals as shown in Figure 1c. A subsequent Diels-Alder crosslink breaks the conjugation and thus prevents a recombination of the two radicals, even after they become mobile solitons upon isomerization. Crosslinking in all cis-transoid $(CH)_x$ is thus directly related to spin generation.

EXPERIMENTAL TECHNIQUES

A few milligrams of cis $(CH)_x$ as prepared by the Shirakawa method were sealed into an ESR quartz tube and the Raman and ESR spectra were taken from the same sample at various stages of the isomerization process. All Raman experiments were performed at liquid nitrogen temperature in an immersion cryostat whereas the ESR spectra were measured at room temperature. The microwave power used in the ESR experiment was less than 4μW for the investigation of the all-cis material in order to avoid signal saturation. The isomerization temperature was kept low (between 45°C and 130°C) since the ESR line width and the Raman signal appeared to be very sensitive to the initial stages of the isomerization process. Raman spectra were excited in the visible spectral range between 4579Å and 6709Å. The analysis of the Raman spectra for the trans polymer was performed in terms of long and short conjugations. A detailed discussion of the Raman data will be given elsewhere.

EXPERIMENTAL RESULTS

Taking Raman spectra at various stages of the isomerization a continous change of the characteristic lines for the cis isomer to those of the trans isomer was observed. In particular the parts of the resonance-enhanced trans lines which originate from the long and the short segments, respectively, were observed to develop as two separate bands. For a quantitative measure for the degree of isomerization, the strong isolated cis line at 1252 cm^{-1} was used. Figure 2 shows the relative change of scattering intensity on a logarithmic scale as a function of isomerization time at 130 C for exitation with 4579Å laser light. The initial isomerization rate R_i appears much higher than the rate R for the later isomerization as indicated in the figure. Performing this analysis for various temperatures revealed an activation energy of 16 kcal/mol and 28 kcal/mol for R_i and R, respectively. This is in good agreement with results

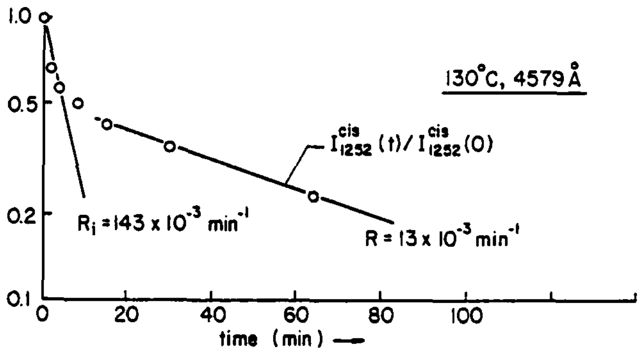

Figure 2. Relative change of scattering intensity of the line at 1252 cm^{-1} in cis CH_x for isomerization at 130 C.

obtained by Shirakawa[16] from infrared studies. It should be noticed that, in the case of Figure 2, isomerization was not yet completed after 65 minutes at 130 C.

A similar analysis can be performed with the trans line for the C = C stretch mode. In order to get isomerization rates, $1 - I^{tr}(t)/\ I^{tr}(0)$ was plotted and results identical to those with the cis line were obtained. However, this trans line can be split into contributions from short and long segments, respectively. It turned out that only the part due to short segments exhibits the very high initial isomerization rate. After some isomerization the rates for short and long segments become approximately equal. The diagram is characteristic of what we have observed for isomerization at other temperatures. The line narrowing (x) is very fast and occurs already in the initial stages of the isomerization whereas spin generation ( ) is slower initially. With increasing isomerization the rate of line narrowing slows down. There is clearly no relationship between actual spin concentration and line width. (Final line widths for the all trans

Figure 3 shows the change of the ESR line width and spin concentration on a logarithmic time scale

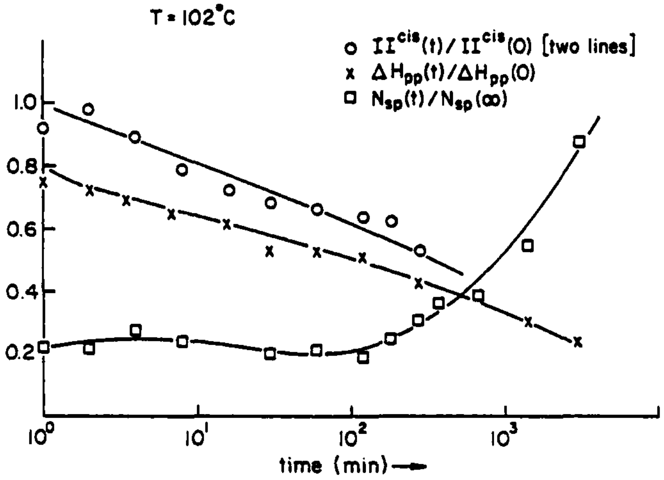

Figure 3. Relative change of ESR line width (x) and spin concentration ( ) for cis-trans isomerization at 102 C as compared to the disappearance of Raman lines from the cis component (o).

material were observed to be between 1.0 and 0.6 gauss depending on the isomerization temperature). The circles (o) represent the normalized cis fraction in the material, as obtained from Raman scattering. Apparently this quantity is directly related only to the ESR line width and not to the spin concentration.

Exciting the Raman spectrum of as-grown cis CH_x with deep red laser light shows a strong enhancement of the scattering intensity from the inevitable small trans content in the sample. This was first observed experimentally by L. Lichtmann[17]. We found that both resonance enhanced lines of the trans polymer develop a detailed fine structure. At least four peaks are present for the band of the

C = C stretch mode. After slight isomerization this band changes rapidly to the well-known triangular form for red light excitation in trans CH_x[6,17]. Figure 4 shows experimental results of Raman spectra for as-grown cis CH_x and slightly isomerized cis CH_x. The top spectrum was excited with 4579Å laser light whereas the two lower spectra were excited with 6709Å laser light. The spectra are normalized to 5mW laser excitation. The resonance-enhanced mode around 1100 cm^{-1} changed in a slightly different way during the isomerization as compared to the pure C = C stretch mode. A detailed study of the change in the band profile and line intensity with isomerization will be published elsewhere*. The structure in the C = C stretch peak was found to be due to resonance scattering from defects on the chain. The resonance condition, the frequency and the change of scattering intensity during isomerization for the peak at 1462 cm^{-1} in the second trace of figure 4 appears as one would expect for a spread-out radical in the cis polymer as e.g. shown in figure 1b and 1c.

DISCUSSION AND CONCLUSION

The very low value of 16 kcal/mol for the activation energy is a clear indication that there must be defect-induced isomerization. As isomerization continues the activation energy increases to 28 kcal/mol. This is already close to the value of 31 kcal/mol observed for other solid polymers with C = C bonds like polyalkenamers.[18] However, in these

---

*We found that the unusual behavior for the excitation of cis CH_x with deep red laser light is due to the different behavior of the optical absorption coefficient for cis and trans CH_x. Since 6709Å is beyond the absorption regime for cis CH_x the small fraction of the latter material is observed in resonance under conditions usually encountered in matrix isolation spectroscopy.

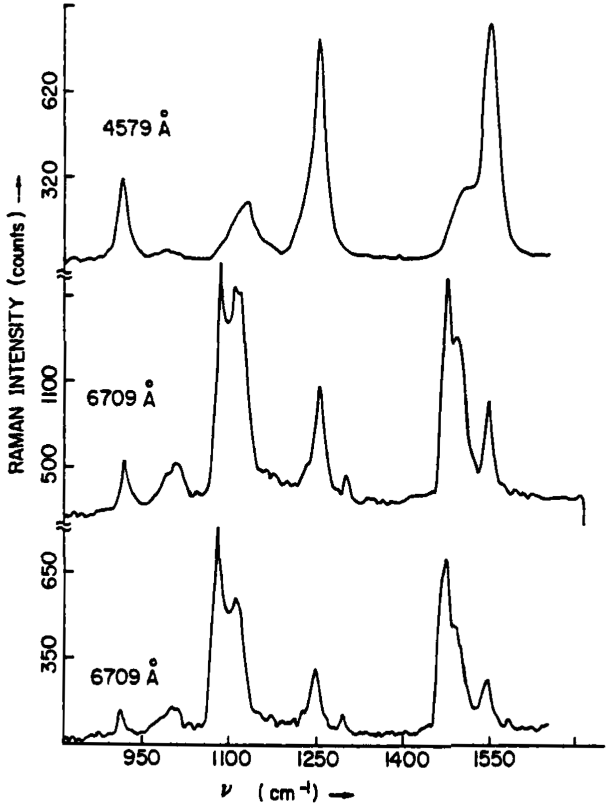

Figure 4. Resonance Raman spectrum for cis CH_x as exicted with 4579Å and for cis CH_x and slightly isomerized cis CH_x (20 minutes at 90 C) as excited with 6709Å. All spectra are normalized to 5 mW excitation.

polymers the process of isomerization is also not well understood. A vibration of the double bond around the dihedral angle might help to lift its strong dien character.[19]

The lack of any direct relation between the generation of spins and the narrowing of the ESR line is clear evidence that exchange interaction is not responsible for the reduction of the line width. The close relation between line narrowing and isomerization suggests rather that the motion of the spins in the isomerized parts of the polymer accounts for the narrowing. Soliton-antisoliton annihilation may be the reason for the reduced net spin generation in the initial steps of isomerization. Annihilation will occur during isomerization whenever two Diels-Alder crosslinks happen to be on the same chain. The Raman band shapes imply the existence of defects in the as-grown cis polymer in general and are consistent with the existence of spread out radicals on the cis parts of the chains in particular. The observed defects may well be the reason for the reduced activation energy for the isomerization process.

In conclusion we found that the model suggested for isomerization and spin generation is capable of explaining detailed results obtained from Raman experiments and from ESR experiments performed during isomerization of CH_x. Spin generation appears thus directly related to cross linking*. The observed narrowing of the ESR line is likely to be due to soliton motion. Defects are observed to play a major role at least in the initial steps of the isomerization process.

ACKNOWLEDGEMENTS

We acknowledge Professor Silsbee for the use of his ESR spectrometer and for valuable discussions. One of us (HK) acknowledges C. Zimm for introducing him to the operation of the spectrometer and acknowledges the Max Kade Foundation for financial

---

*This statement refers only to the pure material. Spin generation and cross linking by impurities, e.g. oxygen, definitely exits as well[20] but need not be related.

support. The work was also partly supported by the National Science Foundation.

REFERENCES

1. Y.W. Park, A.J. Heeger, M.A. Druy and A.G. MacDiarmid, J. Chem. Phys., 73, 946 (1980).
2. B.R. Weinberger, E. Ehrenfreund, A. Pron, A.J. Heeger and A.G. MacDiarmid, J. Chem. Phys., 72, 4749 (1980).
3. M. Nechtschein, F. Devreux, R.L. Green, T.C. Clarke and G.B. Street, Phys. Rev. Lett., 44, 356 (1980).
4. I. Harada, M. Tasumi, H. Shirakawa and S. Ikeda, Chem. Lett., 1411 (1978).
5. S. Lefrant, S.L. Lichtmann, H. Temkin and D.B. Fitchen, Solid State Communications, 29, 191 (1979).
6. H. Kuzmany, Phys. Stat. Sol., (b) 97, 521 (1980).
7. W.P. Su, J.R. Schrieffer and A.J. Heeger, Phys. Rev. Lett. 42, 1698 (1979); Phys. Rev., B21, 1 (1980).
8. Y. Tomkiewicz, T.D. Schultz, M.B. Broom, T.C. Clark and G.B. Street, Phys. Rev. Lett., 43, 1532 (1979).
9. H. Kuzmany, Proc. of the Int. Conf. on Quasi-One Dimensional Conductors, Chemica Scripta, 17, 155 (1981).
10. M.A. Golub, Rubber Chemistry and Technology, 51, 677 (1978).
11. D. Vanderbilt and E.J. Mele, Phys. Rev., B22, 3939 (1980).
12. R.W. Lenz, Organic Chemistry of Synthetic HighPolymers, (Interscience Publishers, New York 1967).
13. G. Wegner, Makromokekulare Chemie, Suppl. 4, 155 (1981).
14. H. Shirakawa and S. Ikeda, J. Polymer Sci., 2, 231 (1971).
15. A. Karpfen and R. Holler, Solid State Communic., 37, 179 (1981).
16. T. Ito, H. Shirakawa and S. Ikeda, J. of Polymer Sc., Polymer Chemistry Ed. 13, 1943 (1975).

17. L.S. Lichtmann, Ph.D. Thesis, Cornell 1981.
18. M.A. Golub, J. Polymer Sc., Polymer Lett. Ed., 12, 295 (1974).
19. T. Yamabe, K. Akagi, K. Ohzeki, K. Fukui and H. Shirakawa, Proc. Int. Conf. on Low Dim. Cond. Boulder 1981, Molecular Cryst. and Liquid Cryst. (to be published).
20. K. Holzer. J.P. Boucher, F. Devreneux and M. Nechtschein, Phys. Rev.,B23, 1051 (1981).