References

1 Patel, A. R. and Usilton, J. J. *Adv. Chem. Ser.* 1978, **169**, 116
2 Shlyapintokh, V. Ya., Ivanov, V. B., Khvostach, O. M., Shapiro, A. B. and Rozantsev, E. G. *Dokl. Akad. Nauk SSSR* 1975, **225**, 1132
3 Carlsson, D. J. International Symposium on Mechanisms of Degradation and Stabilization of Hydrocarbon Polymers, Prague, July 9–12, 1979, *Preprints* p L9
4 Grattan, D. W., Reddoch, A. H., Carlsson, D. J. and Wiles, D. M. *J. Polym. Sci. Polym. Letters. Edn.* 1978, **16**, 143
5 Sedlář, J., Petrůj, J. and Pác, J. International Symposium on Mechanisms of Degradation and Stabilization of Hydrocarbon Polymers, Prague, July 9–12, 1979, *Poster* M47
6 Oswald, A. A., Noel, F. and Stephenson, A. J. *J. Org. Chem.* 1961, **26**, 3969
7 Walling, C. and Heaton, D. *J. Am. Chem. Soc.* 1965, **87**, 48
8 Chien, J. C. W., Vandenberg, E. J. and Jabloner, H. *J. Polym. Sci. A-1* 1968, **6**, 381
9 Denisov, E. T. International Symposium on Degradation and Stabilization of Polymers, Brussels, September 11–13, 1974, *Preprints* p 137
10 Chakraborty, K. B. and Scott, G. *Chem. Ind.* 1978, **1**, 237

E.p.r. study of polyacetylene films

P. Bernier, M. Rolland, C. Linaya and M. Disi

Groupe de Dynamique des Phases Condensées, Laboratoire de Chimie Macromoléculaire and*
Laboratoire de Chimie Structurale Organique, Université des Sciences et Techniques du Languedoc,
Place Eugène Bataillon, 34060 Montpellier Cedex, France

(Received 24 October 1979)

Doped polyacetylene is a material which many laboratories research, and experiments concerning its transport[1–3] and magnetic properties[4–6] have been performed.

Much less work has been done on nondoped samples. Nevertheless, such research can yield interesting information about the origin and nature of the electrons which contribute to the observed electrical conductivity and magnetic susceptibility of nondoped as well as doped samples. We present here an experimental e.p.r. study to check whether unpaired electrons exist in a pure *cis*–$(CH)_x$ polyacetylene isomer and remain during the thermal isomerization from *cis* to *trans*.

Using the method described by Ito *et al.*[7], polyacetylene has been directly prepared at –78°C in the e.p.r. tube which was sealed under vacuum just after termination of polymerization. Using a Bruker ER 10 spectrometer with a variable temperature apparatus, the e.p.r. spectra were immediately recorded at the temperature of polymerization. *Figure 1a* shows that, if there is a very broad, large signal, due in particular to Ti^{3+} ions contained in the catalyst system and centred near $g = 1.95$, no signal exists at the free electron g value 2.0023. The catalyst e.p.r. spectrum, which has been extensively studied[8,9], is known to depend strongly on the characteristics of the catalytic melt (particularly the molar ratio of the constituents $(C_2H_5)_3$ Al and $(n\text{-}C_4H_9O)_4$ Ti, and on the temperature. Our observations are in agreement with other work[8,9].

Increasing the temperature to –18°C drastically changes the form of the spectrum centered at $g = 1.95$ but at the same time a small symmetric signal appears at $g = 2.0023$ (*Figure 1b*). Its width (defined as the distance in gauss between the two peaks of the absorption derivative), which is difficult to measure with accuracy, is of the order of 10 gauss.

A further increase in temperature to 25°C again changes the catalyst signal while the signals in the spectrum near $g = 2.0023$ continues to grow without any significative change in line-width and position (*Figure 1c*). After 15 min at this

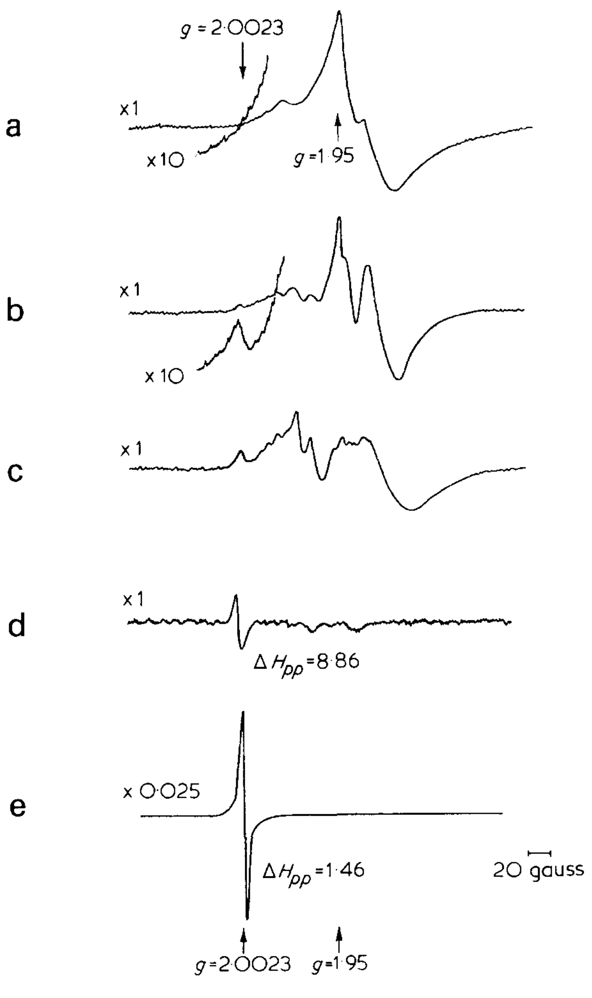

Figure 1 Recorded e.p.r. spectra on polyacetylene and its catalytic system from the temperature at which it has been polymerized to room temperature. While the catalyst signal at $g = 1.95$ disappears by thermal treatment and oxidation, the signal coming from the polyacetylene at $g = 2.0023$ builds up. Its linewidth decreases when the system is heated to 200°C. (a), –78°C; (b), –18°C; (c), 25°C; (d), 25°C, 20 min exposure to air pressure; (e), 25°C, after 1 min heat treatment at 200°C

---

* Laboratoire associé au C. N. R. S.

0032–3861/80/010007–02$02.00

temperature, a small increase of the signal amplitude is induced without any change in line-width. A systematic study of the way the equilibrium is reached at a given temperature is under progress.

When the experiment described is performed on the catalytic system alone, no signal at $g = 2.0023$ is observed, showing that such a signal is connected with the existence of the polyacetylene film.

More information can be obtained by exposure of the sample to air pressure at room temperature. Such a treatment over 20 min yields important modifications: the catalyst signal amplitude goes to zero as Ti^{3+} is oxidized to the non-paramagnetic state Ti^{4+}; simultaneously, the signal at $g = 2.0023$ slightly increases while its width remains constant at 8.8 gauss (*Figure 1d*). An investigation of the effect of oxygen on the spectrum at $g = 2.0023$ is under progress and will be published elsewhere[10].

The sample tube was again sealed under vacuum, and isomerization to the *trans* configuration performed by a heat treatment at 200°C. The e.p.r. spectrum, taken at room temperature, shows a total disappearance of the catalyst signal while the line at $g = 2.0023$ is considerably increased, with a smaller width (1.4 gauss) than in the *cis* case (*Figure 1e*). Nevertheless, the intensity is about 10 times greater than in the *cis* isomer at room temperature, showing that unpaired electrons are created during isomerization.

In view of the preceding results, it is clear that the existence of a signal at $g = 2.0023$ is an intrinsic property of the polyacetylene chain and is correlated with the *trans* content of the system. The *cis* configuration which is formed at −78°C is stable only at this temperature and isomerization starts at the time the conditions are changed and is more and more complete as the temperature is increased.

Unpaired electrons can exist in *trans* sequences of the system due to defects in the double bond conjugation appearing as domain walls or phase kinks[11,12]. Such defects only exist in the case of the *trans* configuration, where the bond alternation can be perturbed without any change in the total energy of the chain; this is not the case with the *cis* configuration[13]. The absence of any hyperfine splitting in the observed e.p.r. spectra is a consequence of the mobility of the unpaired electrons over a given distance of the chains[14]. The narrower spectrum observed with the *trans* isomer only means that *trans* sequences are of greater extent than in the *cis* configuration, leading to a much more efficient 'motional narrowing'.

More detailed experiments are in progress to help understand the mechanism of isomerization at temperatures below room temperature.

Acknowledgement

Many thanks to Professor A. G. McDiarmid for very helpful discussions. Support by Bruker Spectrospin France for the e.s.r. equipment is gratefully acknowledged.

References

1 Chiang, C. K., Park, Y. W., Heeger, A. J., Shirakawa, H., Louis, E. J., Gau, S. C. and McDiarmid, A. G. *Phys. Rev. Lett.* 1977, **39**, 1098

2 Seeger, K., Gill, W. D., Clarke, T. C. and Street, G. B. *Solid State Commun.* 1978, **28**, 873

3 Mihaly, G., Vancso, G., Pekker, S. and Janossy, A. submitted to *Synthetic Metals*

4 Weinberger, B. R., Kaufer, J., Heeger, A. J., Pron, A. and McDiarmid, A. G. to be published; Goldberg, I. B., Crowe, H. R., Newman, P. R., Heeger, A. J. and McDiarmid, A. G. *J. Chem. Phys.* 1979, **3**, 1132

5 Snow, A., Brant, P., Weber, D. and Yang, N. L. *J. Polym. Sci., Polym. Lett. Edn.* 1979, **17**, 263

6 Bernier, P., Rolland, M., Galtier, M., Montaner, A., Regis, M., Candille, M., Benoit, C., Aldissi, M., Linaya, C., Schué, F., Sledz, J., Fabre, J. M. and Giral, L. *J. Phys. (Lett.)* 1979, **40**, L-297

7 Ito, T., Shirakawa, H. and Ikeda, S. *J. Polym. Sci., Polym. Chem. Edn.* 1974, **12**, 11

8 Hirai, H., Katsuma, H., Isamu, N. and Makishima, S. *J. Polym. Sci. (A-1)* 1970, **8**, 147

9 Takeda, M., Iimura, K., Nozawa, Y., Hisatome, M. and Koide, N. *J. Polym. Sci. (C)* 1968, **23**, 741

10 Bernier, P., Rolland, M., Linaya, C., Disi, M., Sledz, J., Fabre, J. M., Schué, F. and Giral, L. to be published

11 Su, W. P., Schrieffer, J. R. and Heeger, A. J. *Phys. Rev. Lett.* 1979, **42**, 1698

12 Rice, M. J. *Phys. Lett.* 1979, **71A**, 152

13 Brédas, J. L. and Delhalle, J. to be published; Yamabe, T., Tanaka, K., Terema-e, H., Fukui, K., Imamura, A., Shirakawa, H. and Ikeda, S. *Solid State Comm.* 1979, **29**, 329

14 Weinberger, B. R., Kaufer, J., Heeger, A. J. and McDiarmid, A. G. to be published