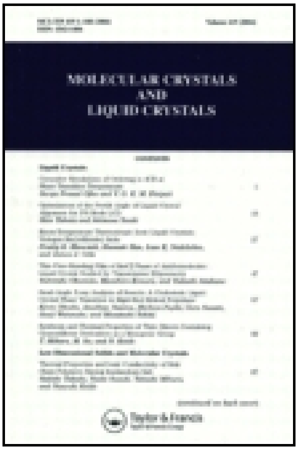
This article was downloaded by: [Tomsk State University of Control Systems and Radio]
On: 20 February 2013, At: 12:49
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Thermal Reactions of Trans-Polyacetylene ESR Kinetics

H. Sixl [a] , H. Hübsch [a] , W. Rühle [a] & S. Roth [b]
[a] Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, 7, Stuttgart 80, Germany
[b] Max-Planck-Institut für Festkörperforschung, 7, Stuttgart 80

Version of record first published: 17 Oct 2011.

To cite this article: H. Sixl , H. Hübsch , W. Rühle & S. Roth (1985): Thermal Reactions of Trans-Polyacetylene ESR Kinetics, Molecular Crystals and Liquid Crystals, 117:1, 479-482

To link to this article: http://dx.doi.org/10.1080/00268948508074669

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:49 20 February 2013

Mol. Cryst. Liq. Cryst. 1985, Vol. 117, pp. 479-482
0026-8941/85/1174-0479/$10.00/0
© 1985 Gordon and Breach, Science Publishers, Inc. and OPA Ltd.
Printed in the United States of America

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:49 20 February 2013

THERMAL REACTIONS OF TRANS-POLYACETYLENE ESR KINETICS

H. SIXL, H. HÜBSCH, W. RÜHLE, S. ROTH*
Physikalisches Institut, Universität Stuttgart,
Pfaffenwaldring 57, 7 Stuttgart 80, Germany
* Max-Planck-Institut für Festkörperforschung, 7 Stuttgart 80

Abstract The high-temperature spin kinetics of trans-polyacetylene in nitrogen and oxygen atmosphere is reported for 300 K T 550 K. The thermal reactions are characterized by S = 1/2 spin generation and annihilation processes. ESR intensities and linewidths are analyzed.

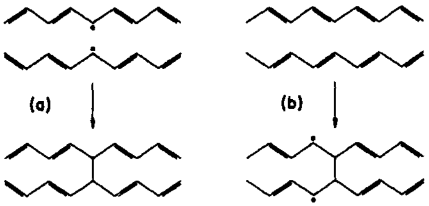
With respect to technological applications one of the main problems of conjugated polymers is their thermal and chemical instability, which has been demonstrated by various experiments[1],[2]. The first detailed ESR-studies of oxygen reactions at room temperature and low-temperatures have been performed by F. Genoud et al.[3],[4]. Two effects due to oxygen adsorption have been observed: a decrease of the ESR intensity and a broadening of the ESR line. In polypyrrol oxygen doping is explained in terms of polaron and bipolaron formation [5]. At temperatures above 300 K in all conjugated polymers chemical reactions with oxygen such as peroxide radical formation, cross-linking and formation of carbonyl groups are expected.

Polyacetylene(PA)-films were prepared following Shirakawa's procedure and isomerized by thermal annealing at 420 K for 30 min in N_2 atmosphere. During the in situ isomerization the ESR line of the S = 1/2 spins becomes purely Lorentzian with ESR linewidth in the order of 0.5 Gauss (at 420 K).

The time dependence of the thermal reaction of the S = 1/2 spins in trans-PA exposed to N_2-atmosphere is shown in Figure 1 by the intensities (a) and linewidths (b) of their ESR signals (c). The total ESR intensity decreases in the thermal reaction. The original narrow line decays, and a transient broad line appears. The activation energies of the spin decay and generation processes are given by 1.5 eV and 1.8 eV, respectively.

The reaction is interpreted by cross-linking, Scheme 1 (a) and (b), reducing the conjugations length of the PA segments. The broadening of the ESR lines thus is a consequence of the restricted mobility of the radical electrons. The activation energy of the spin annihilation involving the reactive S = 1/2 radical electrons (a) is expected to be lower than that of the transient spin generation involving the cleavage of the π-bond (b).

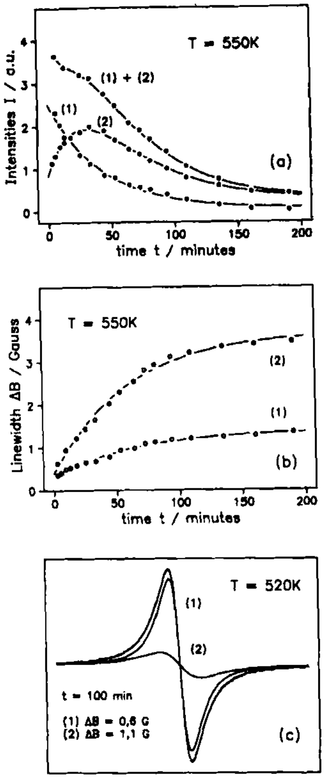
Downloaded by [Tomsk State University of Control Systems and Radio] at 12:49 20 February 2013



Scheme 1:

Cross-linking of the trans-PA chains

a) spin annihilation
b) spin generation



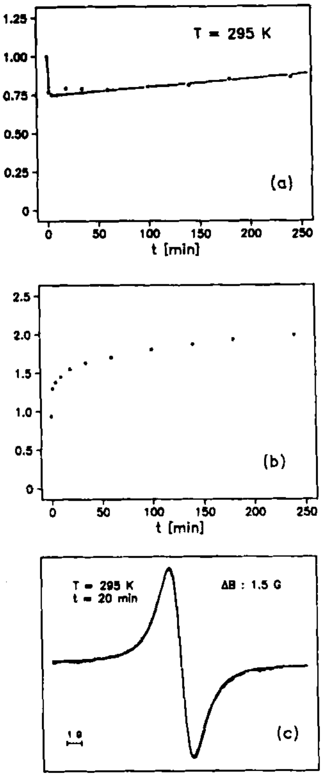


Figure 1: Thermal reactions of the S = 1/2 spins in trans-PA-inert nitrogen atmosphere.
(a) Integrated ESR-intensities (spin concentrations)
(b) ESR-line widths; (c) Simulation of the ESR-line

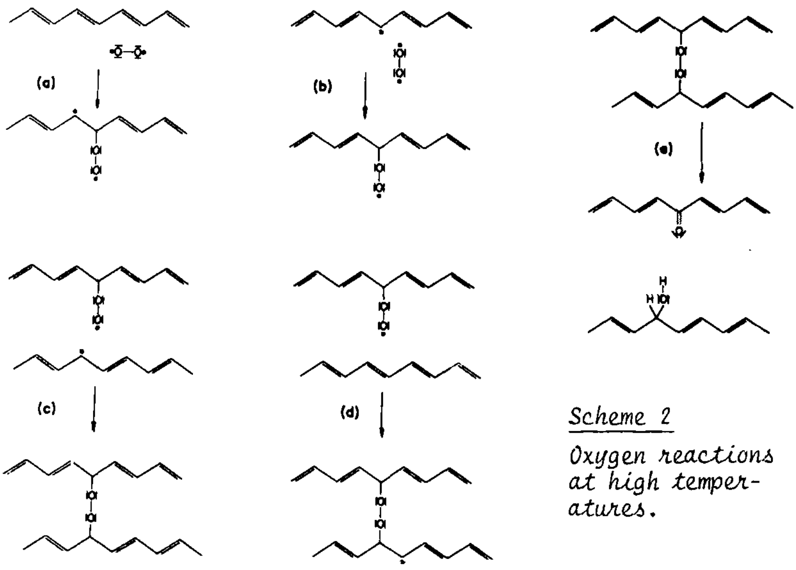
Figure 2: Thermal reactions of the S = 1/2 spins in trans-PA and ambient air - oxygen effects.
(a), (b), (c) see text of Figure 1.

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:49 20 February 2013

The time dependence of the oxygen reactions of the S = 1/2 spins are shown in Figures 2 to 4 for different temperatures. In all cases the reaction is characterized by three essentially different mechanisms. Initially a very fast spin reaction is dominant (Figure 2) followed by an increase and a final decrease of the ESR intensities. The initial fast spin reduction and the subsequent slow spin generation are also present at low temperatures as described by Genoud et al.[3,4]. Only in the initial stage of the reaction the ESR line can be described by a single Lorentzian. All reactions involving spin reduction are partially reversible. Activation energies of 0.45 eV and 0.7 eV of the high temperature spin generation and decay are obtained from Arrhenius plots of the rate constants (Figure 5)

The high-temperature oxygen effects of trans-PA are interpreted by the reactions of Scheme 2. A possible explanation of the spin generation is peroxide formation[3] (a) and peroxide linkage[6] (b). The decay of the spins is interpreted by the reaction (b) and (d). The oxygen linkage is unstable and presumably decays into carbonyl and hydroxy groups (e) as proposed by Gibson and Pochan[2]. As a consequence of the oxygen reactions the mobility of the radical electrons is reduced and the ESR-line broadens.

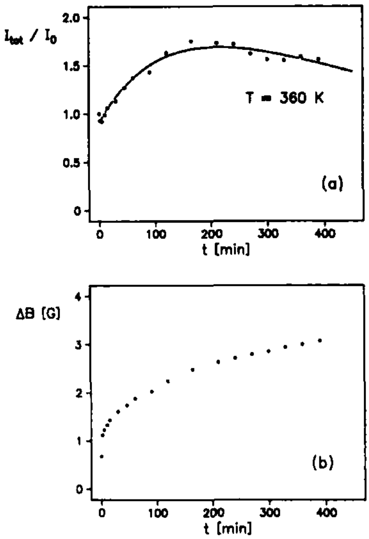
We want to thank K. Menke and K. Ulrich for chemical help in sample preparation and the Stiftung Volkswagenwerk for financial support.



Scheme 2

Oxygen reactions at high temperatures.

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:49 20 February 2013



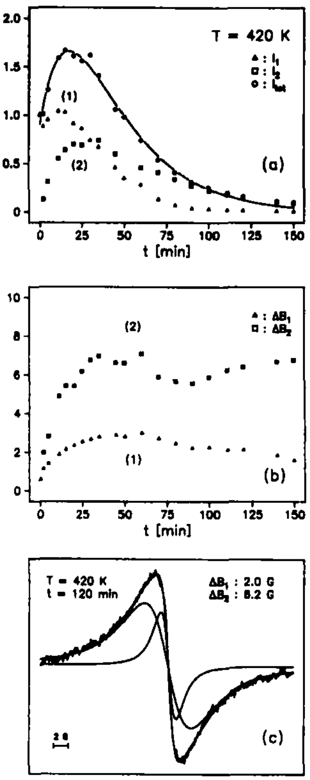


Figure 3 (above) and
Figure 4 (right):
see text of Figure 2

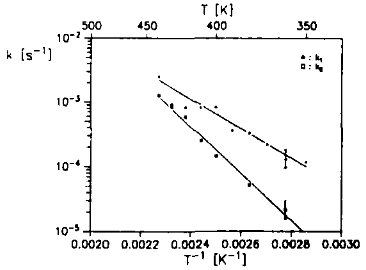


Figure 5 (left):
Temperature dependence of
rate constants

REFERENCES

1. H. Münstedt, H. Naarmann and G. Köhler: these proceedings.
P. Knoll and H. Kuzmany, preprint (1984).
2. H.W. Gibson and J.M. Pochan: Macromol., 15, 242 (1982).
3. F. Génoud, M. Nechtschein, K. Holcer, F. Devreux and
M. Guglielmi: Mol. Cryst. Liq. Cryst., 96, 161 (1983).
4. F. Génoud, F. Devreux, M. Nechtschein and J.P. Travers:
Journal de Physique, supplement au no. 6, 44, C3-291, (1983).
5. J.C. Scott, J.L. Brédas, J.H. Kaufmann, P. Pfluger, G.B. Street
and K. Yakushi: these proceedings.
6. K. Ulrich, private communication.