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Synthesis and e.p.r. studies of polyacetylene hydrogen sulphate $|CH(HSO_4)_y|_x$

F. Rachdi and P. Bernier
Groupe de Dynamique des Phases Condensées, USTL, Place Eugène Bataillon,* 34060 *Montpellier, France*

and D. Billaud
Université de Nancy I, Laboratoire de Chimie du Solide Minéral, Service de Chimie Minérale Appliquée, C.O.* 140, 54037 *Nancy Cedex, France*

and A. Pron and J. Przyluski
Department of Chemistry, Technical University of Warsaw, Warszawa, Noakowskiego 3, *Poland*

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Introduction

Sulphuric acid, H_2SO_4, is known to react with graphite and other macromolecular systems like polyacetylene $(CH)_x$. In the first case reaction occurs only after electrochemical oxidation of graphite[1]. In the latter case reaction occurs directly between the H_2SO_4 vapour and polyacetylene[2]. In a previous study we found[2,3,4] that nitryl and nitrosyl ions (NO_2^+ and NO^+) are excellent species for oxidizing π-systems of graphite and polyacetylene concomitantly introducing anions (e.g. BF_4^-, PF_6^-, SbF_6^-) which stabilize the polycation formed. Recently we have established that a similar reaction can occur between graphite and nitrosyl hydrogen sulphate[5] ($NOHSO_4$). In this communication we want to present recent results concerning the interaction between polyacetylene and nitrosyl hydrogen sulphate.

Experimental and Results

The polyacetylene used in all experiments was prepared by a modification of the method of Ito *et al.*[6]. All-*trans* films of thickness $\sim 100\ \mu$ were used in the experiments. The doping reaction was carried out in the following manner: $NOHSO_4$ (Alfa-Ventron) was placed in the side arm of the reactor and pumped overnight in order to remove the volatile products of the hydrolysis. Then, rigorously dry nitromethane was vacuum distilled into the side arm. The suspension of $NOHSO_4$ in nitromethane was then discharged over the polyacetylene film. The reaction was complete when the characteristic golden colour of the doped polyacetylene could be observed. The excess salt was removed by washing with pure nitromethane and then the film was dried by dynamic pumping.

For the samples doped to saturation the *RT* conductivity measured by a 4-probe, pressure contact, method was 430 $\Omega^{-1}\ cm^{-1}$. The results of elemental analysis, of the same sample, were as follows: $\%C = 46.47$; $\%H = 5.44$; $\%S = 14.29$; $\%N = 1.01$; $\%O$ (by difference) $= 32.79$.

They agreed with the following empirical formula

$$|CH(HSO_4)_{0.12}(CH_3NO_2)_{0.02}|_x$$

The samples for e.p.r. studies (~ 2 mg) were placed in vacuum sealed tubing equipped additionally with a side arm allowing the cryogenic pumping. The e.p.r. spectra were recorded using a conventional X-band spectrometer working at a low hyperfrequency power level (< 1 mW). The temperature of the sample was varied in the range 20°C to 160°C.

For all measurements above room temperature the samples were cryogenically pumped while in the cavity.

Figure 1a presents a typical spectrum obtained at room temperature for an all-*trans* film. The observed symmetric shape as well as the values $g \sim 2.0026$ and $\Delta H_{pp} \sim 1$ G, respectively for the position and the width of the line, agree with standard results[8].

After doping to saturation the observed e.p.r. spectrum has a position which is roughly unchanged, but the line becomes strongly non symmetric (*Figure 1b*). This last property can be characterized by the ratio A/B of the amplitudes A and B measured on the low and high magnetic field sides of the line respectively. After the doping A/B is in the order of 6 and remains constant with time.

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* Laboratoires Associés au C.N.R.S.

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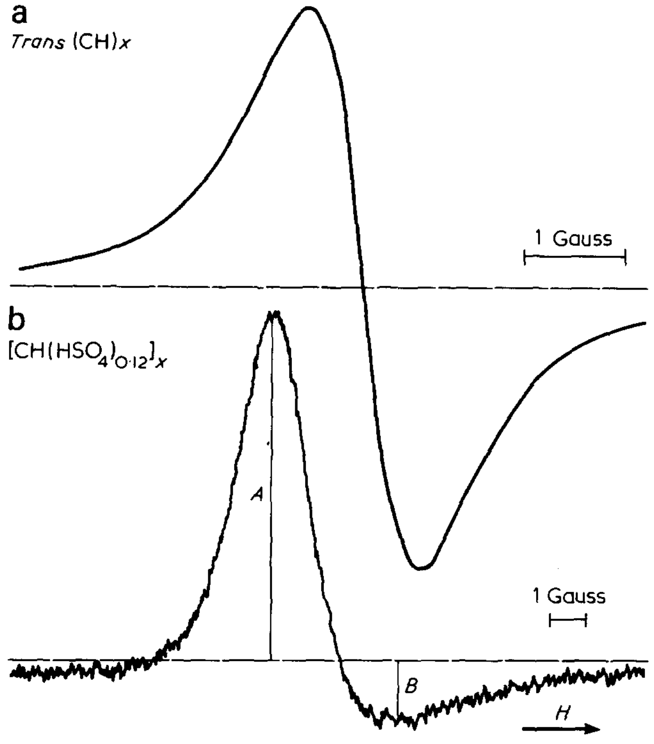

Figure 1 E.p.r. spectra of undoped all *trans* $(CH)_x$ (a) and the same film doped to saturation with $NOHSO_4$ (b)

If the temperature of the sample is increased to 80°C the value $A/B \sim 6$ remains approximately constant. At 100°C we observe a slow and continuous decrease of A/B down to 1.4 after 4 h (*Figure 2*). A further increase in the temperature then induces only a small decrease of A/B. A temperature as high as 160°C is needed to return to an almost symmetric spectrum. On returning to *RT* the A/B ratio remains almost unchanged (close to 1).

Discussion

The nature of dopant species in the case of H_2SO_4 doped polyacetylene is poorly understood and neither the mechanism of doping nor the nature of the dopant after the reaction with the polymer can be established from the data presented in ref. 2. In the case of $NOHSO_4$ doping chemical analysis shows that HSO_4^- is the anion stabilizing the chain which is of polycationic nature *i.e.*:

$$(CH)_x + 0.12 \times NO^+HSO_4^- + 0.02 \times CH_3NO_2 \rightarrow$$

$$|CH^{0.12+}(HSO_4^-)_{0.012}(CH_3NO_2)_{0.02}|_x + 0.12 \times NO\uparrow$$

As can be seen from the analytical data, the solvation of the anion by the molecules of the solvent (CH_3NO_2) occurs only to a very small extent. This is the major difference between the oxidation of $(CH)_x$ and graphite with $NOHSO_4$. In the case of graphite we observe the solvation of each HSO_4^- anion with two solvent molecules *i.e.* $C_n^+HSO_4^-$. 2 CH_3NO_2 [5]. The results are consistent with our previous studies[3,7]: the solvation of anions by solvent molecules was not observed in the reaction of $NOPF_6$ and $NOSbF_6$ with $(CH)_x$ whereas it was observed in the case of graphite.

The *RT* conductivity value of $NOHSO_4$ doped polyacetylene measured in this research is almost 3 times smaller than the values obtained for H_2SO_4 doped polyacetylene for the same doping level. This seems to indicate that different dopant species are introduced into $(CH)_x$ in both cases. The characterization of these species is now in progress.

The e.p.r. results described above are understood in the light of the Dyson theory for metallic plates[9]. In the case of our metallic doped polyacetylene films the skin depth

$$\delta = \frac{c}{2\pi\sqrt{\sigma f}}$$

(c = speed of light; σ = conductivity; f = hyperfrequency value) is of the order of 25 μ, which is four times smaller than the thickness of the sample. In such a case we expect an important asymmetry of the spectrum under the form observed in *Figure 1b*. Nevertheless it is difficult to make a quantitative analysis of such a shape, since our material is fibrilic and fibers do not fill the space uniformly[7] and spin diffusion is highly anisotropic[10].

After doping with $NOHSO_4$ the number of observed unpaired spins N_s, deduced from the e.p.r. intensity, decreases by one order of magnitude if compared with the parent $(CH)_x$. We note firstly that, due to the metallic state of the system, this number is only a fraction of the total number of spins contained in the whole sample: the higher the conductivity, the smaller N_s. In contrast with our present results, other authors have observed an increase of N_s upon doping with AsF_5 [11], and the reasons for such differing behaviour is not clearly understood. Secondly we point out the fact that the exact origin of the observed spins after doping is still unclear, which does not allow us to expect any behaviour, at least in the case of high level doping.

After thermal treatment at 160°C, N_s (measured at room temperature) has practically recovered the value it had for the parent $(CH)_x$. This result indicates that the doping and dedoping processes do not significantly perturb the diffusive properties of the unpaired electrons along the chains. We have even noted after the thermal treatment an e.p.r. linewidth of 0.45 G, *i.e.* two times

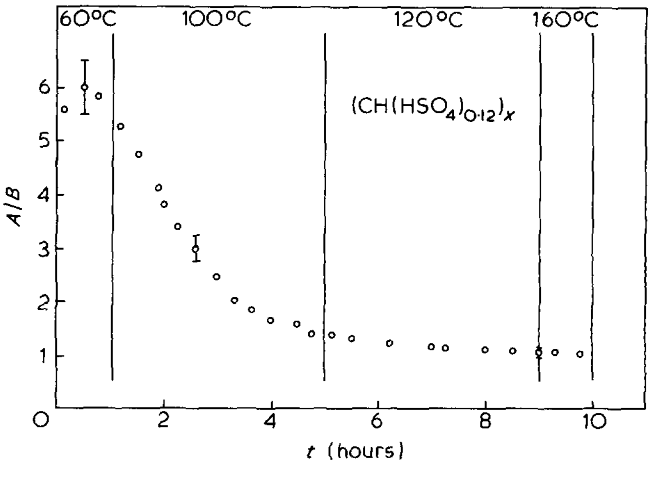

Figure 2 Asymmetry ratio A/B defined on *Figure 1b*, plotted *versus* time at different temperatures for $(CH)_x$ doped with $NOHSO_4$. Between each vertical line the temperature is constant. The heating rate between each constant temperature measurement was ~10°C min^{-1}

smaller than for the parent $(CH)_x$. The origin of such a difference is not understood at this time.

The variation with time and temperature of the A/B ratio (*Figure 2*) is a good test of the stability of the doped system. Up to 80°C the constant A/B ratio indicates no significant change in the conductivity. At higher temperatures A/B decreases as the conductivity decreases, due to the loss of dopant. As a reference we have observed that with a conductivity of the order of 5 $(\Omega\ \mathrm{cm})^{-1}$ the e.p.r. spectrum was symmetric. The observation of a slight asymmetry even after a few hours at 120°C ensures that the system has a conductivity higher still than ~ 10 $(\Omega\ \mathrm{cm})^{-1}$. We note that in the present case the stability is largely improved if compared with iodine doped $(CH)_x$ for which the metallic state disappears above 80°C [12].

In conclusion we can say that doping polyacetylene (CH_x) with $NOHSO_4$ leads to a highly conducting material. The metallic state has been characterized using e.p.r. and has been shown to be reasonably stable with time at temperatures below ~120°C.

Acknowledgement

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Synthesis and characterization of tetramethyl-*p*-silphenylene siloxane/dimethylsiloxane multiblock copolymer

Yu Nagase, Tetsuo Masubuchi, Koji Ikeda and Yoshiro Sekine
Department of Chemistry, Waseda University, Okubo, Shinjuku-ku, Tokyo, Japan

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Introduction

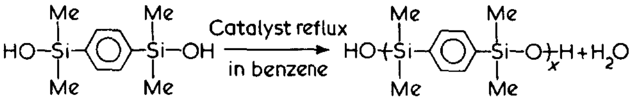
Tetramethyl-*p*-silphenylenesiloxane/dimethylsiloxane (TMPS/DMS) block copolymers have been synthesized by the polycondensation of *p*-bis(dimethylhydroxysilyl)benzene (TMPS monomer) and silanol-terminated dimethylsiloxane oligomers by Merker and his co-workers[1]. These kinds of block copolymers have been regarded as comprising two segments, one of which is poly-TMPS as the hard segment and the other is poly-DMS as the soft segment. The chemical degradations[2,3], crystallization kinetics[4,5], thermal properties[6], mechanical properties[7] and morphology[8-10] of the block copolymers have been investigated in detail by Magill *et al.*, and it is found that they are thermoplastic elastomers. However, because in their method, TMPS monomers were randomly condensed to form TMPS segments in the copolymers, a constant TMPS segment length could not be obtained. Therefore, it might be important to clarify the effects of TMPS and DMS segment length on the thermal and mechanical properties of the block copolymers which have the apparent segment length.

Pittman *et al.* carried out the preparation of alternating poly(arylenesiloxane) by the hetero-functional condensation of bis-silanols with bis-aminosilanes to obtain highly viscous silicone oils having functional groups[11]. Furthermore, O'Malley *et al.* studied the synthesis and characterization of alternate poly(hexamethylenesebacate)-poly(dimethylsiloxane) (AB)*n* type block copolymers by the coupling reactions of the terminal hydroxy groups of hexamethylenesebacate and either of the chlorosilyl- or dimethylaminosilyl-terminal groups on DMS.

This communication describes the synthesis of alternating (AB)r type TMPS/DMS block copolymers by the polycondensation of silanol-terminated TMPS oligomers and dimethylamino-terminated DMS oligomers, and their thermal properties.

Experimental

Preparation of silanol-terminated TMPS oligomer. The preparation method of Merker *et al.*[13] was used. According to equation (1), *p*-bis(dimethylhydrosylsilyl)benzene (20g) was polymerized in benzene (40 ml) in the presence of n-hexylamine 2-ethylhexoate (0.1 g) acting as catalyst using an azeotrope trap to remove water. In the course of the condensation reaction, water separated in the azeotrope trap was measured to control the molecular weights of the oligomers. The oligomers obtained were reprecipitated in methanol to remove the catalyst. The number-average molecular



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