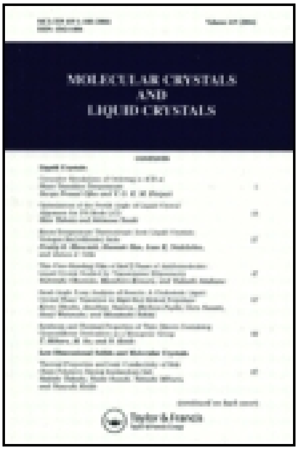

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

New ldopants converting polyacetylene, $(CH)_x$ into a metal: Ferric, aluminium and zirconium chlorides

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Version of record first published: 14 Oct 2011.

To cite this article: I. Kulszewicz , D. Billaud , A. Pron , P. Bernier & J. Przyluski (1982): New ldopants converting polyacetylene, $(CH)_x$ into a metal: Ferric, aluminium and zirconium chlorides, Molecular Crystals and Liquid Crystals, 83:1, 159-164

To link to this article: http://dx.doi.org/10.1080/00268948208072166

Mol. Cryst. Liq. Cryst., 1982, Vol. 83, pp. 159–164
0026-8941/82/8301–0159$06.50/0

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

NEW DOPANTS CONVERTING POLYACETYLENE, $(CH)_x$ INTO A METAL : FERRIC, ALUMINIUM AND ZIRCONIUM CHLORIDES

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Received for publication September 4, 1981

The reactions of $FeCl_3$, $AlCl_3$ and $ZrCl_4$ dissolved in nitromethane with $(CH)_x$ result in the formation of p-type conducting polymers. Of all three new materials $FeCl_3$ doped $(CH)_x$ exhibits the highest conductivity and stability in air. EPR shows a broad line which is consistent with high spin Fe^{2+} complex formed in the reaction. $AlCl_3$ doped samples are also highly conducting but very unstable in air. The EPR spectrum is only slightly Dysonian probably due to the partial reaction of the dopant with traces of moisture. $ZrCl_4$ dopes $(CH)_x$ to significantly lower conductivity giving a weak totally symmetric EPR signal.

INTRODUCTION

Recently we have found[1,2] that $FeCl_3$ can convert polyacetylene $(CH)_x$ and polyparaphenylene $(C_6H_4)_x$

into highly conducting materials. Mössbauer studies show that in the case of polyacetylene a complete reduction of Fe^{3+} to Fe^{2+} occurs, and Fe^{2+} high spin complex (probably $FeCl_4^{2-}$) is formed in this process. Elemental analysis is consistent with this formulation. In this paper we present additional metal chlorides ($AlCl_3$, $ZrCl_4$) capable to oxidize the π system of polyacetylene leading to the formation of highly p-type conducting polymers.

EXPERIMENTAL

Films of polyacetylene were synthesized by the modification of the method of Ito et al.[3] using $Al(C_2H_5)_3/Ti(OC_4H_9)_4$ Ziegler-Natta system. All three chlorides were heated under dynamic vacuum at 100°C for one hour before use to remove volatile hydrolysis products. Cis-rich (60 %) films of $(CH)_x$ were doped using saturated solutions of $FeCl_3$, $AlCl_3$ and $ZrCl_4$ in dry nitromethane. After the reaction was completed the excess of salt was washed out using pure nitromethane and the solvent was removed by extended ca. 12 hours pumping. Doped samples were transferred into EPR tubing under inert atmosphere. The EPR spectra were recorded at room temperature using a home made spectrometer working at 9.4 GHz with a low hyperfrequency power (< 2 mW). Conductivity measurements were performed at room temperature using a standard four probe pressure contact method.

RESULTS

The results of conductivity measurements are listed in Table 1. Upon exposure to air the conductivity of $FeCl_3$ doped $(CH)_x$ decreases slowly being still metallic even after 120 hours ($\sigma \sim 200\ (\Omega\,cm)^{-1}$). The weight changes measurements during the first few minutes exposure to air show an unsignificant increase of the mass of the sample at the level of micrograms. On the contrary air stability of the $AlCl_3$ doped material is strikingly smaller. The sample conductivity and its mass change drastically during the

TABLE 1 Room Temperature Conductivities of Metal Chlorides Doped $(CH)_x$

Compound	Conductivity $(\Omega \, cm)^{-1}$
$(CH(FeCl_3)_{0.10})_x$ [a]	780
$(CH(AlCl_3)_{0.06})_x$ [b]	250
$(CH(ZrCl_4)_y)_x$ [c]	5

[a] Composition determined by mass uptake

[b] Composition determined by combustion analysis

[c] No composition known

first few minutes of exposure to air.

The EPR spectra for the three doped systems are shown in Figure 1. In the case of $ZrCl_4$ we observe a single symmetric line whose g-value (~ 2.0026) and width (~ 5.6 Gauss) are similar to those of the parent polyacetylene[4]. In the case of $AlCl_3$ doping the observed single line exhibits the features typical of the parent $(CH)_x$ but is slightly asymmetric with an asymmetry ratio (high field peak amplitude / low field peak amplitude) close to 1.2. A completely different magnetic resonance behaviour is observed in $FeCl_3$ doped $(CH)_x$. The EPR asymmetric signal is extended over more than 2000 Gauss and its g-value cannot be clearly defined.

DISCUSSION

A very broad EPR signal observed for $FeCl_3$ doped $(CH)_x$ is characteristic of all paramagnetic iron complexes[5]. The absence of any signal corresponding to parent $(CH)_x$ indicates homogeneous interfibrillar distribution of the dopant, but it does not prove the homogeneity of the dopant distribution within the fiber since the resonance of any remaining neutral magnetic defect should be removed by the interaction with paramagnetic environ-

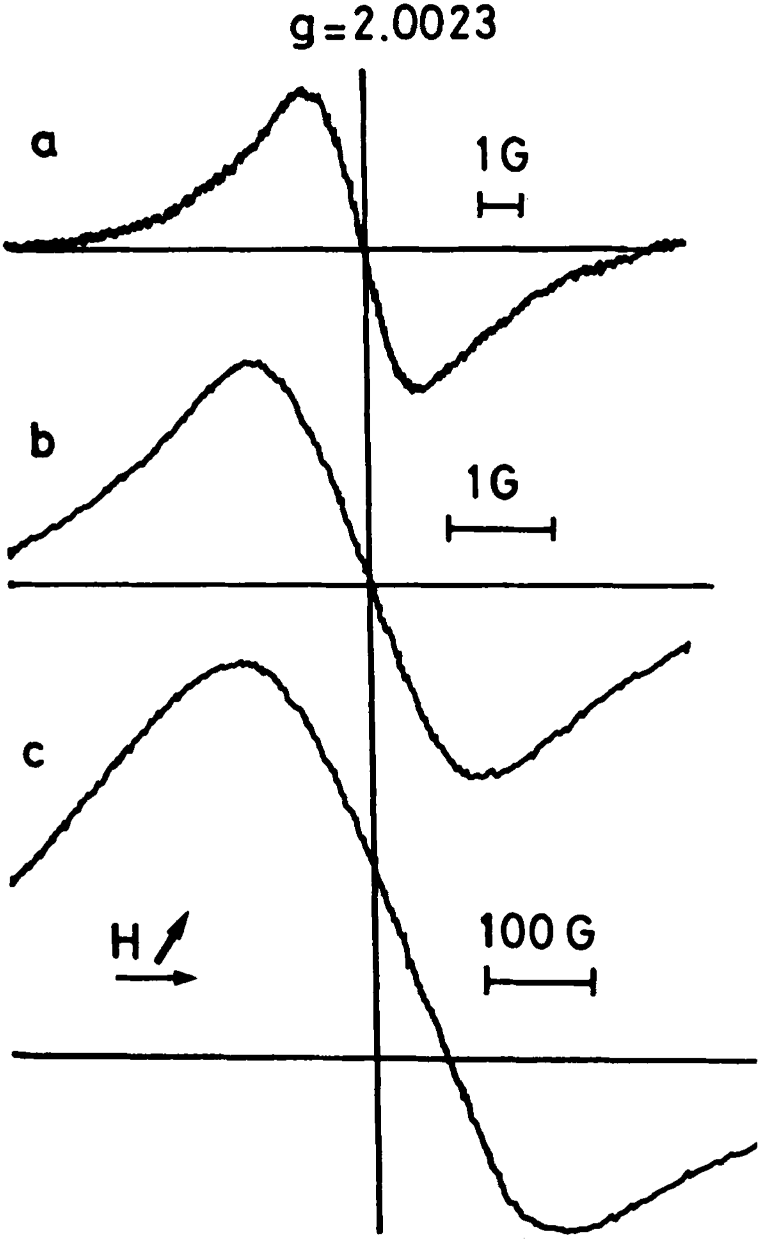

FIGURE 1 Room temperature EPR spectra of $(CH(ZrCl_4)_y)_x$ (a), $(CH(AlCl_3)_{0.06})_x$ (b) and $(CH(FeCl_3)_{0.1})_x$ (c). Vertical units are arbitrary

ment.

The EPR results are consistent with our previous Mössbauer and elemental analysis studies[1,2] in which we postulated that $FeCl_4^{2-}$ is the dopant species in $FeCl_3$ doped $(CH)_x$.

Tetrahedral $FeCl_4^{2-}$ is a very well known Fe^{2+} high spin complex. It is stable in air when stabilized by large cations (for example in quaternary salts of the type $(R_4N)_2FeCl_4$ [6]. Therefore we can conclude that slow degradation of $FeCl_3$ doped $(CH)_x$ in air is associated rather with the instability of the polymeric cation towards the attack of oxygen and water than the instability of the anion.

The doping of polyacetylene with $AlCl_3$ requires at least partial charge transfer from the polymer to the dopant in order to create free carriers. It is well known that aluminium compounds in the oxidation state lower than III are unstable. Under such conditions one should expect that any charge transfer from the polymer chain to the dopant molecules will lead to the unstable product with respect to the anion as well as the cation.

The EPR results are consistent with the idea of the partial charge transfer since the product is diamagnetic and only a weak signal associated with parent $(CH)_x$ can be seen as it is usually observed for other diamagnetic dopants [7,8]. The exact nature of the dopant after the doping reaction is not known at the present time.

It is surprising that the EPR signal of heavily (6 %) $AlCl_3$ doped $(CH)_x$ is only slightly unsymmetric despite the high conductivity observed in freshly doped samples. The possible explanation is that minute amount of moisture adsorbed on the walls of EPR tubing could react with the film lowering its conductivity. It is highly likely in view of the fact that the mass of samples taken for EPR is very small (ca. 2 mg).

The EPR signal for $ZrCl_4$ doped $(CH)_x$ is totally symmetric, in agreement with considerably lower conductivity of the sample. The reaction product is diamagnetic consistent with Zr^{4+} oxidation state. The weak EPR signal can be attributed to parent $(CH)_x$.

ACKNOWLEDGMENTS

The authors wish to thank the Centre National de la Recherche Scientifique for partial financial support (ATP grant).

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