

## New Fast and Easy Procedure for n-Doping Polyacetylene with $H_4LiAl$ as the Electron Donor. A Method for Producing Polyene Anions

Jean-Marie Dohan, Stéphane Boué,\* and Emile Vander Donckt\*

*Collectif de Chimie Organique Physique, Faculté des Sciences, Université Libre de Bruxelles, 50, Av. F. D. Roosevelt, B-1050 Bruxelles, Belgium*

It has been shown unambiguously that lithium aluminium hydride in tetrahydrofuran solution reduces polyacetylene to the poly-anionic n-semiconducting state with concomitant escape of gaseous hydrogen.

Although  $H_4LiAl$  is universally known as a hydrogen donor, there is one reported case of polyaromatic hydrocarbon reduction proceeding by electron transfer from the hydride.<sup>1</sup> We have now discovered that this also applies to polyacetylene  $(CH)_x$ .

Polyacetylene films (0.5  $\mu\text{m}$  thick) were prepared following Shirakawa's procedure.<sup>2</sup> The samples absorb light in the visible region with  $\lambda_{\text{max}}$  ca. 600 nm. As an  $H_4LiAl$ -THF solution (THF=tetrahydrofuran) is introduced into the cell the film slowly turns blue and after a period of 10 min the original absorption band vanishes and a new broad absorption develops, extending beyond 1800 nm and with a shallow maximum at 1300 nm, which is assigned to polyene radical anions with metal counter-cations. At the same time, a gas evolves. Addition of water quickly bleaches the blue colour but displaces the original  $\pi^* \leftarrow \pi$  transition of polyacetylene down to 480 nm. These observations are consistent with the production of polyene anions by electron transfer from  $H_4LiAl$  and concomitant release of hydrogen. On the basis of this assumption we undertook a quantitative study of the process using finely powdered samples of polymer.

Upon treatment with a  $H_4LiAl$ -THF solution, powdered dry outgassed *trans*-polyacetylene reacts vigorously, producing  $H_2$  according to rather complex thermally activated kinetics which depend on the hydride concentration and on the polymer sample. Subsequent treatment of that polymer with  $D_2O$ , after removal of the excess of  $H_4LiAl$ , results in the release of a  $D_2$ -HD mixture and a time-dependent analysis

of the  $D_2$ :HD ratio shows that  $D_2$  is produced first in a fast reaction followed by slower evolution of HD. The production of HD demands that metal-hydrogen bonds be still present in the washed polymer, *i.e.* the four hydrogens from the hydride have not all been used up in the electron transfer process. The i.r. spectrum of the polymer recovered after hydrolysis exhibits a weak C-D stretching absorption at 2150  $\text{cm}^{-1}$ , which means that addition of  $D^+$  on carbon competes with the  $D_2$ -producing reduction. Reduction of  $(CH)_x$  with  $D_4LiAl$  followed by hydrolysis with  $H_2O$  shows no detectable incorporation of deuterium, *i.e.* reduction proceeds exclusively through electron transfer and addition only occurs upon hydrolysis. From the mass spectrometric analysis of the  $D_2O$ -HOD- $H_2O$  mixture obtained by total combustion of a doped sample hydrolysed with  $D_2O$ , the gross formula  $C_{30}H_{30}D$  is deduced. This corresponds to a 20% average yield of  $D^+$  addition on carbon and 80% yield of  $D_2$  released. On the basis of the amount of  $D_2$  or  $H_2$  evolved per gram of polyacetylene, we found that the mean anion charge density is typically ca.  $(CH^{0.2-})_x$  (*i.e.* 2 electrons per 5 double bonds) but can be as high as  $(CH^{0.94-})_x$ , depending on both the hydride concentration and the quality of the polymer; this implies that the doped material is largely poly-anionic or even quasi-metallic. This remarkably high charge density suggests that  $H_4LiAl$  could be a suitable reagent for preparing the anions of relatively short conjugated polyenes.

Our primary concern being the formation of n-doped semi-conducting polyacetylene, we wanted to ensure that the reduc-

tion achieved with  $\text{H}_4\text{LiAl}$  actually leads to the same n-doped species as that obtained by treatment with melted sodium or with sodium naphthalide.<sup>3</sup> Two gold electrodes were deposited 0.1 cm apart from each other on polymer films *ca.* 20  $\mu\text{m}$  thick and 1 cm wide; after doping, the THF solvent was removed to avoid ionic conduction and a conductivity of 6  $\Omega^{-1}\text{cm}^{-1}$  was measured. Thus the hydride proves to be an n-doping agent that is at least as good as sodium naphthalide. There are various advantages in using  $\text{H}_4\text{LiAl}$  rather than sodium naphthalide. Among them is the release of  $\text{H}_2$  which provides a quantitative determination of the anions produced and a source of irreversibility for the electron transfer process.

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