

## New Charge Transfer Complexes between Tetracyanoethylene (TCNE) and Conducting Polymers (Polyacetylene and Polypyrrole)

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Polyacetylene and polypyrrole, conjugated polymers, were treated with a TCNE–AlCl<sub>3</sub>–benzene solution and converted into conducting materials, leading to the formation of partial electron transfer  $\pi$ -complexes and to the substitution of TCNE onto the pyrrole rings, as shown by e.s.r. and <sup>13</sup>C n.m.r. spectroscopy.

It has been shown that conjugated polymers can be substantially changed by means of n- or p-type doping.<sup>1</sup> Doped polymers exhibit semiconductor or metallic levels of conductivity, depending on the concentration of the dopant. Several groups of inorganic electron acceptor-type dopants have been established for polyacetylene and polypyrrole. We present reactions of conjugated polymers (*i.e.* polyacetylene and polypyrrole) with an organic electron acceptor: tetracyanoethylene (TCNE), in the presence of AlCl<sub>3</sub>. TCNE is a strong  $\pi$ -acid forming numerous weak  $\pi$ -complexes<sup>2,3</sup> as well as anion-radical salts.<sup>4</sup>

A (CH)<sub>x</sub> film prepared by the method of Ito *et al.*<sup>5</sup> was doped with TCNE–benzene and TCNE–AlCl<sub>3</sub>–benzene solutions at room temperature. The resultant films were washed with pure benzene. Polypyrrole-1 was prepared by chemical oxidation of pyrrole in an ethanol–aqueous solution containing iron(III) chloride. The dried black precipitate was reduced with a Na<sup>+</sup>(C<sub>10</sub>H<sub>8</sub>)<sup>-</sup>-tetrahydrofuran (THF) solution to obtain a yellow, low-conducting polymer and subsequently it was immersed in a TCNE–AlCl<sub>3</sub>–benzene solution. Black polypyrrole-2, thus obtained, was washed with pure benzene and vacuum dried.

The i.r. spectrum of polyacetylene doped with the TCNE–benzene solution shows the two soliton modes at 1370 and *ca.* 900 cm<sup>-1</sup>. The increase and subsequent decrease of absorption level in the i.r. spectrum show that the Diels–Alder addition of TCNE to the polymer chain, which is in competition with weak  $\pi$ -complex formation, may occur. The spectrum of the (CH)<sub>x</sub> film that was obtained after a long reaction time exhibits the  $\nu$ (C $\equiv$ N) vibration mode at 2190 cm<sup>-1</sup> [shifted with respect to the 2260, 2220 cm<sup>-1</sup>  $\nu$ (C $\equiv$ N) doublet of pure TCNE] and the weak C–C mode at 1135 cm<sup>-1</sup> (1155 cm<sup>-1</sup> in TCNE spectrum) overlapping with the (CH)<sub>x</sub>

fundamental mode (1115 cm<sup>-1</sup>). The conductivity of this polymer remains low (10<sup>-5</sup>  $\Omega$ <sup>-1</sup> cm<sup>-1</sup>).

The reaction of (CH)<sub>x</sub> with a TCNE–AlCl<sub>3</sub>–benzene solution increases the polymer conductivity to *ca.* 8  $\Omega$ <sup>-1</sup> cm<sup>-1</sup> [for *trans*-(CH)<sub>x</sub>,  $\Delta m/m_0$  (mass increase after doping) = 48%]. Higher values of conductivity for the *trans*-(CH)<sub>x</sub> isomer were obtained [65% *cis*-(CH)<sub>x</sub>,  $\sigma = 9 \times 10^{-2}$   $\Omega$ <sup>-1</sup> cm<sup>-1</sup>,  $\Delta m/m_0 = 30.8\%$ , 95% *trans*-(CH)<sub>x</sub>,  $\sigma = 2$   $\Omega$ <sup>-1</sup> cm<sup>-1</sup>,  $\Delta m/m_0 = 30\%$ ]. The conductivity of (CH)<sub>x</sub> immersed in the AlCl<sub>3</sub>–benzene solution remains in the range 10<sup>-5</sup>  $\Omega$ <sup>-1</sup> cm<sup>-1</sup>.

The X-ray photoelectron spectrum of (CH)<sub>x</sub> doped with TCNE shows the presence of carbon, nitrogen, chlorine, aluminium, and oxygen. The binding energy of C(1s) is equal to 284.2 eV and this value is comparable with the C(1s) energy of polypyrrole as can be expected.<sup>6</sup> The binding energy of N(1s) is equal to 398.1 eV and differs from the value 409.9 eV obtained for physically adsorbed gaseous nitrogen. The N(1s) energy of our compound is red-shifted with respect to the N(1s) energy of conducting polypyrrole.<sup>6</sup> This value is compatible with the energy shift proposed for deprotonated nitrogen in polypyrrole.<sup>7</sup> Apart from the main peak, a shoulder is found to its high binding energy side.

The e.s.r. study of *trans*-(CH)<sub>x</sub> doped with TCNE–AlCl<sub>3</sub>–benzene and TCNE–benzene solutions shows a single Lorentzian-shape signal. The Lande factor *g* is equal to 2.0028, the value of  $\Delta H_{pp}$  decreases (with increasing conductivity) from 1.34 G for pure *trans*-(CH)<sub>x</sub> to 0.56 for highly doped *trans*-(CH)<sub>x</sub>.† No other paramagnetic signal has been observed in a spectrum of doped (CH)<sub>x</sub>. Moreover, in the case of both TCNE–benzene and TCNE–AlCl<sub>3</sub>–benzene solutions no signal was found.

† 1 G = 10<sup>-4</sup> T.

(CH)<sub>x</sub> doped with the TCNE–AlCl<sub>3</sub>–benzene solution was placed in a NaI–MeCN mixture and a yellow solution was obtained. The u.v.–visible (600–220 nm) spectrum of this solution differs from the spectrum of TCNE–NaI–MeCN solution, but is similar to the TCNE–AlCl<sub>3</sub>–NaI–MeCN spectrum. The yellow solution exhibits a strong paramagnetic signal ( $\Delta H_{pp} = 8.04$  G) characteristic of radical species. The e.s.r. spectrum has no hyperfine structure contrary to the NaI–TCNE–MeCN spectrum.<sup>4</sup> We have concluded that TCNE forms a weak  $\pi$ -complex with (CH)<sub>x</sub>. AlCl<sub>3</sub> interacts either with  $\pi$ -electrons of TCNE or with the lone pair of electrons of the nitrogen atoms. This interaction increases the electron transfer from the polyacetylene to the TCNE molecule.

A different reaction of the TCNE–AlCl<sub>3</sub>–benzene solution occurs in the case of polypyrrole. A non-conducting reduced form of polypyrrole was converted into the conducting black material. The reaction is more complex than in the case of (CH)<sub>x</sub>. The magic-angle high resolution <sup>13</sup>C n.m.r. spectrum of polymer-1 contains a main peak at  $\delta$  128.9 characteristic of the pyrrole ring carbon and a shoulder at a lower chemical shift value. The peak shoulder may be caused by carbon atoms of the pyrrole ring binding to methyl groups. The presence of methyl groups was observed at  $\delta$  18.0. No n.m.r. spectrum for polymer-2 was found. We suppose that TCNE has been substituted into the pyrrole rings replacing the hydrogen atoms. Polymer-2 shows an e.s.r. signal with a *g*-factor equal to 2.0026 and  $\Delta H_{pp} = 0.7$  G. The i.r. spectrum of polypyrrole-2 is similar to that of polymer-1, but a strong  $\nu(\text{C}\equiv\text{N})$  mode at 2220 cm<sup>-1</sup> was observed. The 1480 cm<sup>-1</sup> pyrrole ring vibration mode of polypyrrole-1 was shifted to

1375 cm<sup>-1</sup> in the spectrum of polymer-2. Unexpectedly, peaks at 1040, 930, and 770 cm<sup>-1</sup> caused by C–H in-plane and C–H out-of-plane deformations,<sup>8</sup> respectively, were observed.

The reactions of a TCNE–AlCl<sub>3</sub>–benzene solution with (CH)<sub>x</sub> and polypyrrole differ from other doping reactions and are significantly different from each other. Doping molecules form weak partial electron transfer complexes with (CH)<sub>x</sub>. On the other hand TCNE molecules are substituted into the pyrrole rings of polypyrrole and the formation of weak  $\pi$ -complexes of TCNE with the polymer chains cannot be excluded.

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