

## AlCl<sub>3</sub>-ASSISTED FORMATION OF CHARGE-TRANSFER COMPLEXES BETWEEN POLYACETYLENE AND TETRACYANOETHYLENE, TCNE

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### Abstract

Polyacetylene, (CH)<sub>x</sub>, the simplest conjugated polymer, can be converted into a conducting material ( $8 \Omega^{-1} \text{ cm}^{-1}$ ) by treating it with a TCNE/AlCl<sub>3</sub>/benzene solution. An electron transfer  $\pi$ -complex was obtained, as shown by EPR and XPS spectroscopies.

**Keywords:** charge transfer complex, polyacetylene doping, tetracyanoethylene

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### Introduction

The electrical conductivity of polyacetylene, a semiconducting polymer, can be changed by a doping reaction with a large variety of electron-accepting or electron-donating compounds. The conductivity level depends on the dopant concentration. Electron-accepting dopants involve the oxidation of the polymer chain with the concomitant introduction of an appropriate amount of anions to stabilize the polycarbonium cation. There are several groups of inorganic compounds capable of oxidizing polyacetylene. They can be classified as follows: halogens [1], metal halides [2], noble gas fluorides [3] and protonic acids [4].

We present the reaction of polyacetylene with a new kind of p-type dopant-organic electron-acceptor, *i.e.*, tetracyanoethylene (TCNE). TCNE is a strong  $\pi$ -acid forming numerous weak  $\pi$ -complexes [5] as well as anion-radical salts [6], but it is a poorer electron-accepting agent than commonly known inorganic dopants.

### Experimental

The polyacetylene used in all experiments was prepared by a modified method of Ito *et al.* [7]. *Cis-trans* isomerization at 200 °C for 5 min was executed. TCNE was sublimed before use. Benzene was dried by metallic

sodium and vacuum distilled.  $\text{AlCl}_3$  was sublimated at  $200^\circ\text{C}$  in vacuum and in a chlorine atmosphere. 0.05 M TCNE and 0.002 M  $\text{AlCl}_3$  in benzene solution were used for polyacetylene doping. The resultant  $(\text{CH})_x$  film was washed with pure benzene and vacuum dried.

The infrared spectra were obtained using a Perkin-Elmer 782 infrared spectrophotometer.

The XPS spectra were recorded using a vacuum scientific generator MK2 Escalpe (Surface Science Company) with monochromatized Al  $K\alpha$  or Mg  $K\alpha$  radiations and an energy resolution of 0.7 eV. The pressure during the measurements was maintained at  $\sim 10^{-9}$  Torr by ionic pumps.

EPR measurements were carried out on a Bruker ER-200 D spectrometer at 9.8 GHz.

Conductivity measurements were carried out *in situ* in the reaction vessel using a standard four-probe technique. Electrode or silver contacts were applied before the reaction.

## Results

The i.r. spectrum of polyacetylene doped with a TCNE/benzene solution shows two soliton modes at 1370 and  $\approx 900\text{ cm}^{-1}$ . In the initial period of reaction, the absorption level increases over the whole recorded spectral range. After a 20 h period, the absorption level decreases. The  $(\text{CH})_x$  film, which was reacted for three days, exhibits a  $\nu(\text{C}\equiv\text{N})$  vibration mode at  $2190\text{ cm}^{-1}$ . This mode is thus shifted with respect to the 2260 and  $2220\text{ cm}^{-1}$  vibration doublet observed in the pure TCNE spectrum. A weak C—C mode at  $1135\text{ cm}^{-1}$  ( $1155\text{ cm}^{-1}$  in the TCNE spectrum) overlapping with the  $1115\text{ cm}^{-1}$   $(\text{CH})_x$  fundamental mode was found. The conductivity of this polymer still remains low ( $10^{-5}\text{ }\Omega^{-1}\text{ cm}^{-1}$ ).

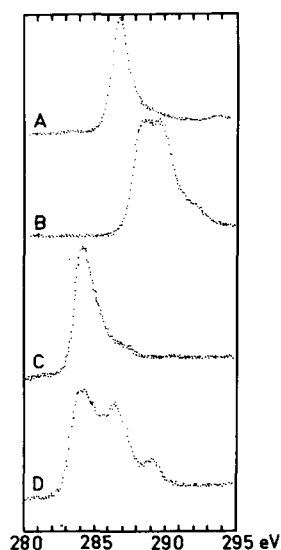
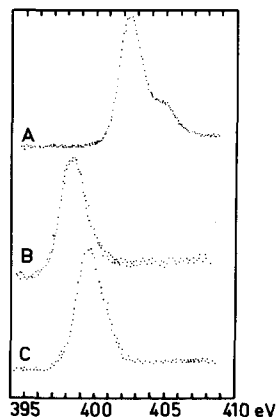
The treatment of  $(\text{CH})_x$  with TCNE/ $\text{AlCl}_3$ /benzene solution results in the increase of the polymer conductivity to  $\approx 8\text{ }\Omega^{-1}\text{ cm}^{-1}$  (for 95% *trans*- $(\text{CH})_x$ ,  $\Delta m/m_0 = 48\%$ ). Higher values of conductivity were obtained for *trans* than for *cis* isomer. For a 65% *cis*- $(\text{CH})_x$  sample doped to  $\Delta m/m_0 = 30.8\%$ , the conductivity was equal to  $9 \times 10^{-2}\text{ }\Omega^{-1}\text{ cm}^{-1}$ . For a 95% *trans*- $(\text{CH})_x$  sample doped to  $\Delta m/m_0 = 30\%$ , the conductivity increases to  $2\text{ }\Omega^{-1}\text{ cm}^{-1}$ . The conductivity of  $(\text{CH})_x$  immersed in an  $\text{AlCl}_3$ /benzene solution remained around  $10^{-5}\text{ }\Omega^{-1}\text{ cm}^{-1}$ .

The XPS wide-range spectrum of  $(\text{CH})_x$  doped with a TCNE/ $\text{AlCl}_3$ /benzene solution exhibits the presence of carbon, nitrogen, aluminum, chlorine and oxygen. The C 1s spectrum is unsymmetric and the main peak is centred at 284.1 eV (sample 1, Table 1 and Fig. 1). A superposition of the three most significant peaks at 284.1, 286.4 and 289.0 eV in the C 1s spectrum of sample 2 was found. The C 1s binding energy of doped  $(\text{CH})_x$  was less than the relative energies for pure  $(\text{CH})_x$  and TCNE. The N 1s binding energy of doped  $(\text{CH})_x$  differs considerably from the 409.9 eV obtained for physically adsorbed gaseous nitrogen. The N 1s spectrum is

TABLE 1

XPS results of polyacetylenes and TCNE

No	Sample	C 1s (eV)	N 1s (eV)	Al 2p (eV)	Al 2s (eV)	Cl 2p (eV)	O 1s (eV)	$\sigma$ ( $\Omega^{-1} \text{ cm}^{-1}$ )
1	(CH) <sub>x</sub>	286.8						$10^{-7}$
2	TCNE	288.3 289.5	402.5					
3	Sample 1 <sup>a</sup> ( $\Delta m/m_0 = 7\%$ )	284.1	398.4		118.2	198.5		0.1
4	Sample 2 <sup>a</sup> ( $\Delta m/m_0 = 29.7\%$ )	284.1 286.4 289.0	399.6	74.8	119.4	199.2	532.3	0.33
5	Sample 3 <sup>a</sup> ( $\Delta m/m_0 = 9\%$ )	288.9	404.9	80.3	125.1	204.5		$2 \times 10^{-4}$

<sup>a</sup>(CH)<sub>x</sub> doped with TCNE/AlCl<sub>3</sub>/benzene solution.Fig. 1. XPS C 1s spectra of (A) (CH)<sub>x</sub>; (B) TCNE; (C) (CH)<sub>x</sub> doped with TCNE/AlCl<sub>3</sub>/benzene solution (sample 1); (D) (CH)<sub>x</sub> doped with TCNE/AlCl<sub>3</sub>/benzene solution (sample 2).Fig. 2. XPS N 1s spectra of (A) TCNE; (B) (CH)<sub>x</sub> doped with TCNE/AlCl<sub>3</sub>/benzene solution (sample 1); (C) (CH)<sub>x</sub> doped with TCNE/AlCl<sub>3</sub>/benzene solution (sample 2).

red-shifted with respect to the N 1s energy of pure TCNE (Fig. 2). Apart from the main peak, a shoulder in the N 1s spectrum of doped (CH)<sub>x</sub> exists in its high binding energy wing. The values of the Al 2s, Al 2p and Cl 2p binding energies of doped (CH)<sub>x</sub> are comparable with the respective energies

of pure  $\text{AlCl}_3$ . For sample 3, each of the peaks is shifted by  $\approx +0.5$  eV with respect to those of sample 2.

Elemental analyses do not give reliable results due to the high reactivity of the samples. They generally show the presence of the expected elements C, H, N, Al, Cl, but in additional significant amounts of oxygen are present. The presence of oxygen and an H/C ratio higher than one suggest partial hydrolysis of the sample. This hydrolysis is further corroborated by the low Cl/Al ratio ( $< 3$ ). However, the TCNE/ $\text{AlCl}_3$  ratios are in the range one to four depending on the TCNE and  $\text{AlCl}_3$  concentrations in benzene.

Some EPR spectra of *trans*-(CH)<sub>x</sub>, pure and doped with TCNE/benzene or TCNE/ $\text{AlCl}_3$ /benzene solutions, were obtained. All spectra show a single Lorentzian-shape signal. The Lande factor  $g$  is equal to 2.0028;  $\Delta H_{pp}$  has a tendency to decrease from 1.40 G for pure *trans*-(CH)<sub>x</sub> to 0.56 G for highly-doped *trans*-(CH)<sub>x</sub> (Table 2). The  $\Delta H_{pp}$  value of *trans*-(CH)<sub>x</sub> doped with the TCNE/benzene solution is greater than that of pure *trans*-(CH)<sub>x</sub>. In the case of both TCNE/benzene and TCNE/ $\text{AlCl}_3$ /benzene solutions, no signal was found.

TABLE 2

EPR results of polyacetylene doped with TCNE/ $\text{AlCl}_3$ /benzene solution

$\Delta m/m_0$ (%)	$g$	$\Delta H_{pp}$ (G)	$\sigma$ ( $\Omega^{-1} \text{ cm}^{-1}$ )	$d$ -thickness ( $\mu\text{m}$ )
0	2.0028	1.40	$10^{-5}$	140
12	2.0028	1.05	0.8	140
38.6	2.0028	0.56	1.3	140
50 <sup>a</sup>	2.0029	1.54	$10^{-5}$	130

<sup>a</sup>(CH)<sub>x</sub> doped with TCNE/benzene solution.

TABLE 3

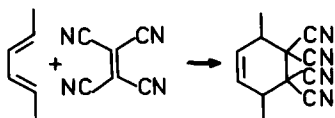
U.v./vis measurements of TCNE solutions

TCNE/ $\text{CH}_3\text{CN}$ (nm)	TCNE/ $\text{NaI}/\text{CH}_3\text{CN}$ (nm)	Solution 1 (nm)	$\text{NaI}/\text{TCNE}/\text{AlCl}_3/\text{CH}_3\text{CN}$ (nm)
414.2	414.2		
397.3	323.8		
		361	361.9
301.1	292.6	291.5	292.6
266		256	
258		251.6	
251.6	249.5	245.8	247.0
246	246		
	244.2		
240.4		240.5	

In order to verify whether the identity of TCNE was retained during the reaction, a polyacetylene sample doped with a TCNE/ $\text{AlCl}_3$ /benzene solution was immersed in a  $\text{NaI}/\text{CH}_3\text{CN}$  mixture and a yellow solution 1 was obtained. The u.v./vis (600 - 220 nm) spectrum of this solution shows peaks at 361, 291.2 and  $\approx 248$  (256, 251.6, 245.8, 240.5 nm). The first one corresponds to the 361.9 nm peak of a TCNE/ $\text{AlCl}_3$ / $\text{NaI}/\text{CH}_3\text{CN}$  solution (Table 3). The first peak of the TCNE/ $\text{NaI}/\text{CH}_3\text{CN}$  solution appears at 383.8 nm with a shoulder at 414.2 nm. The EPR spectrum of yellow solution 1 shows a strong signal ( $\Delta H_{pp} = 8.04$  G) characteristic of radical substances. The spectrum has no hyperfine structure, contrary to that of  $\text{NaI}/\text{TCNE}/\text{CH}_3\text{CN}$  [6].

## Discussion and conclusions

The doping reaction causes an oxidation (p-type doping) or a reduction (n-type doping) of the  $\pi$ -electron system in the polyacetylene chains. The charge introduced exists in the form of charged solitons. Two strong vibrational modes at 1370 and  $\approx 900$   $\text{cm}^{-1}$  in the i.r. spectrum are associated with the presence of solitons. We have observed the same modes in the i.r. spectrum of  $(\text{CH})_x$  reacted with a TCNE/benzene solution. It can be said that in this case a charge transfer complex is formed. The decrease and subsequent increase of the absorption level in the i.r. spectrum as well as the increase of the  $\Delta H_{pp}$  value of  $(\text{CH})_x$  doped with a TCNE/benzene solution with respect to the  $\Delta H_{pp}$  value of pure *trans*- $(\text{CH})_x$  suggest that Diels-Alder addition of TCNE to the polymer chains can occur. This reaction competes with the  $\pi$ -complex formation process. The Diels-Alder addition can be described by the following reaction:



In this case we can note the formation of  $\text{C sp}^3$  defects in the polymer chain and a decrease of the conductivity. The conductivity of this sample remains low ( $10^{-5} \Omega^{-1} \text{ cm}^{-1}$ ). The addition of  $\text{AlCl}_3$  to the TCNE/benzene solution changes the reaction system. The conductivity of  $(\text{CH})_x$  reacted with the TCNE( $\text{AlCl}_3$ /benzene solution increases by several orders of magnitude to  $8 \Omega^{-1} \text{ cm}^{-1}$ . One can suppose that  $\text{AlCl}_3$  participates in the  $(\text{CH})_x$ -TCNE complex formation, as was confirmed by elemental analysis, XPS and u.v./vis measurements. Also the possibility of Diels-Alder addition in this case cannot be excluded. The conductivity values were lower for the *cis* than for the *trans* isomer and it seems that Diels-Alder addition is easier in the *cis* case.

The calculation of the relative elemental concentrations suggests that an adduct of the type  $\text{CH}(\text{C}_6\text{H}_4)_y(\text{AlCl}_3)_2$  is formed, which undergoes quick

hydrolysis even in the presence of a minute amount of water. This hydrolysis significantly lowers the Cl/Al ratio in the elemental analysis.

The XPS studies of doped  $(\text{CH})_x$  show that the C 1s binding energy is comparable to the C 1s energy of conducting polypyrrole [8] and this value is red-shifted with respect to the C 1s energies of pure  $(\text{CH})_x$  and TCNE, respectively. However, we cannot compare the absolute values because of the different sample conductivities. One can only note that the charge accumulated in sample 3 is greater than that in sample 2. The dissymmetry of the C 1s spectrum is caused by the molecules of TCNE bonded with the polymer and by the C  $\text{sp}^3$  defects in the polyacetylene chains. We conclude that the wide 286.4 eV peak in the spectrum of highly-doped sample 2 is caused by the C 1s doublet of TCNE molecules. The low-intensity 289.0 eV peak can be caused by polymer carbon atoms bonded with oxygen. The rapid degradation of doped  $(\text{CH})_x$  after air exposure was confirmed by the conductivity measurements. The N 1s energy of doped  $(\text{CH})_x$  is red-shifted with respect to the energy of pure TCNE and the conducting polypyrrole [8] (samples 1, 2). We cannot conclude that this is due to an electron environment of nitrogen atoms because of a different charge accumulated in the samples. The low-intensity shoulder in the N 1s spectrum could be connected with partial degradation of the sample and with possible protonation of nitrogen atoms.

The EPR spectra show the single Lorentzian-shaped signal caused by the unpaired electrons (neutral solitons) of the polymer. No paramagnetic signal characteristic of an anion-radical was observed. We suppose that a complex with partial electron transfer is formed. It can be found in the ground-state singlet. The complex formation energy is relatively low and the triplet state complex cannot be populated thermally (as in the case of the benzene-TCNE complex [9]). Only a triplet-state complex can dissociate to form polycarbocation and TCNE anion-radical. The low  $(\text{CH})_x$ -TCNE complex formation energy was confirmed by EPR studies of solution 1. The TCNE slightly bonded with  $(\text{CH})_x$  chain was reacted with a  $\text{NaI}/\text{CH}_3\text{CN}$  solution and  $\text{TCNE}^{\pm}$  was obtained. The comparison of EPR and u.v./vis results indicates that there is a contribution of  $\text{AlCl}_3$  to the  $(\text{CH})_x$ -TCNE and  $\text{Na}^+\text{TCNE}^{\pm}$  formations.  $\text{AlCl}_3$  can interact either with the  $\pi$ -electrons of TCNE or with the lone pair of nitrogen atom electrons (the  $\text{CN}-\text{AlCl}_3$  adducts are well known [10]).

The reaction of polyacetylene with TCNE/ $\text{AlCl}_3$ /benzene solution differs from other p-type doping. The TCNE does not induce a complete oxidation of the polymer chain, but partial electron transfer from  $(\text{CH})_x$  into the acceptor molecule occurs. This process provokes the conductivity increase of several orders of magnitude. The contribution of  $\text{AlCl}_3$  in the complex formation was noticed.

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