Highly conducting polymers based on polyacetylene hydrogen sulphate: Preparation and stability studies

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Oxidation of polyacetylene with sulphuric acid, leading to the formation of highly conducting polymer films, was studied under varying conditions. It was found that the highest quality films were obtained in the gas phase reaction with 98% H_2SO_4 where the H_2SO_4/H_2O ratio is crucial for correct doping. The reaction product can be formulated as $[CH(HSO_4)_y]_x$. Oxygen attack leads to the irreversible degradation of the polyene chain and reaction with H_2O results in compensation of the dopant anions.

Keywords Sulphuric acid oxidation; polyacetylene; *p*-type doping; highly conducting polymer; stability studies

INTRODUCTION

Sulphuric acid is known to react with polyacetylene to give highly conducting films displaying *p*-type conductivity[1,2]. Similar systems such as nitrosyl hydrogen sulphate also oxidize polyacetylene, producing films with essentially identical properties[3].

The mechanism proposed in the literature for the $(CH)_x$–H_2SO_4 reaction involves the addition of proton to the double bond leading to the formation of the polycation and subsequent insertion of the corresponding number of anions to preserve the charge neutrality of the product[1]. Since the addition of each proton introduces a sp^3 defect into the polyene chain a severe decrease of the conjugation length should therefore be expected upon doping. Therefore it does not seem probable that the above postulated reaction can cause a significant conductivity increase. To the contrary it should convert a conjugated semiconducting system into a partially saturated insulating system, especially for high doping levels.

The literature data concerning doping conditions and stoichiometry of the product are unclear. The only formula presented in the literature $[CH(H_2SO_4)_{0.016}(H_2O)_{0.07}]_x$[1] merely represents the results of combustion analysis and by no means corresponds to the proposed mechanism.

The aims of this work were:

(i) to find the optimum doping conditions;

(ii) to determine the real stoichiometry of the compound formed after doping and to establish the chemical nature of the dopant species;

(iii) to explain the reasons for the instability of the product.

EXPERIMENTAL

Films of $(CH)_x$ and $(CD)_x$ were polymerized from C_2H_2 and C_2D_2 using the $AlEt_3/Ti(OBu)_4$ catalytic system as described by Ito *et al.*[4]. For gas-phase oxidation experiments, H_2SO_4 was degassed at 80°C for 2 h using dynamic pumping and then a strip of polyacetylene (2 cm × 0.5 cm × 0.005 cm) was mounted in a 4-probe configuration parallel to the surface of the liquid acid phase at varying distances. Finally the system was pumped at room temperature in a vacuum line and the changes of mass of the sample were measured periodically. Selected samples were subjected to elemental analysis. H_2SO_4 concentrations varying from 95% to 99% were used in the experiments. For the stability studies undoped or doped $(CH)_x$ was exposed to the vapours of deoxygenated water or dry oxygen.

I.r. spectra were recorded in air using a Specord 75 IR spectrometer (GDR production).

RESULTS AND DISCUSSION

Two main features of the polyacetylene oxidation with sulphuric acid are:

(i) Oxidation rate and maximum doping level depend strongly on the concentration of the acid used. Gas-phase doping rate decreases gradually if the concentration is lowered from 98 to 95%. Below 95% the reaction becomes extremely slow and insignificant.

(ii) The geometry of the reactor plays a key role in the doping process. Only dynamically pumped samples placed in close proximity (*ca.* 0.5 cm) parallel to the surface of the H_2SO_4 phase can be doped effectively. Cryogenic pumping seems to be ineffective. Doping in liquid sulphuric acid[5] leads to samples of poor quality and will therefore not be discussed here.

On exposure to air the doped film undergoes a significant change as manifested by its mass increase. Elemental analyses presented in *Table 1* show the continuous increase of H/C and O/C ratios with exposure time.

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Table 1 Elemental analyses of H_2SO_4 doped $(CH)_x$*

	Calculated**	Found	
		I	II
C	40.83	39.06	38.50
H	3.97	5.23	5.47
S	18.40	17.53	17.20
O***	36.80	38.18	38.83
C/H	1/1.169	1/1.61	1/1.70

* Two parts of the same sample, kept in air for 3 and 10 min respectively, were analysed

** Calculated from mass increase of the sample weighed in dry argon assuming the formula $[CH(HSO_4)_y]_x$

*** Calculated as %O = 100 − Σ C,H,S

In order to establish the correct formula of the doped film the following experiment was carried out: In a dry argon atmosphere a piece of freshly doped $(CH)_x$ was placed in a polyethylene envelope of known mass and sealed. The two were then combusted together in the microanalyser. An identical empty polyethylene envelope was combusted as a reference. Typical results are presented in *Table 2*. Within the experimental error the H/C ratio obtained corresponded to the formula $[CH(HSO_4)_y]_x$.

The mass increase in air is accompanied by an electrical conductivity decrease. Conductivity studies are helpful in establishing which of the main components in air are responsible for the conductivity drop. The results of such studies are presented in *Figure 1*. In the experiment a strip of $(CH)_x$ doped to 8.5% was cut into three identical pieces with the first piece being exposed to air, the second to 1 atm of dry O_2 at room temperature and the third to the saturated vapour pressure of water at room temperature in the vacuum line. In the case of H_2O, only three experimental points were taken since the appearance of the ionic component of the conductivity severely perturbed the measurements and extended pumping was required prior to measurement, to remove the source of the ionic conductivity. The action of pure oxygen on $[CH(HSO_4)_y]_x$ produces irreversible mass increase that cannot be removed on pumping. The product of the reaction of $[CH(HSO_4)_y]_x$ with H_2O vapour must be slightly volatile since the mass of the film decreases upon pumping and slowly approaches the mass of the original undoped $(CH)_x$.

It may be stated therefore that the interactions of oxygen and water with polyacetylene hydrogen sulphate are of a different nature, the first probably being associated with the polymer chain, the second with the dopant anion. The negative effect on conductivity is much more pronounced in the case of H_2O exposure than in the case of O_2. These results have prompted us to examine the degradation reaction by i.r. spectroscopy.

Table 2 Analysis of H_2SO_4 doped $(CH)_x$ combusted in polyethylene envelope

	pe	pe + pa + H_2SO_4
%C	86.45	72.72
%H	13.82	10.01
Mass taken mg	2.48	4.38
C/H	1/1.92	1/1.65

* C/H ratio in the product calculated from the combustion analysis = 1/1.10

** C/H ratio in the product calculated from the mass increase assuming $[CH(HSO_4)_y]_x$ = 1/1.12

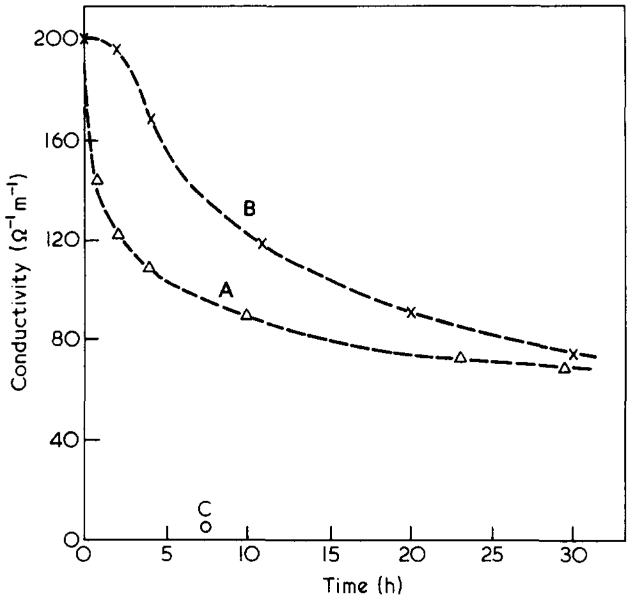

Figure 1 Conductivity *versus* exposure time for different degrading agents: A, exposed to air; B, exposed to 1 atm. of dry oxygen; C, exposed to 17.5 Torr of deoxygenated water

In view of all the results collected above it seems clear why the doping reaction is so strongly dependent on the geometry of the reactor (in particular on the distance between the sample and the source of vapours) and on the H_2SO_4/H_2O ratio in the acid used. Let us examine the absolute values of p_{H_2O} and $p_{H_2SO_4}$ being in equilibrium with liquid acid phase. At room temperature the $(p_{H_2O} + p_{H_2SO_4})$ value is *ca.* 1.10^{-4} Torr and decreases with the increase in acid concentration[6,7]. For the optimum doping rate the conditions for molecular flow must be achieved and this is possible by minimizing the distance between the substrate and the source of vapours and by effective dynamic pumping leading to a vacuum well below 10^{-4} Torr. In view of the reaction of water with $[CH(HSO_4)_y]_x$ accompanied by the quick conductivity drop, the ratio $p_{H_2SO_4}/p_{H_2O}$ in the vapour phase becomes important. The absolute value $(p_{H_2SO_4} + p_{H_2O})$ decreases upon the acid concentration increase, but at the same time the $p_{H_2SO_4}/p_{H_2O}$ ratio changes from *ca.* 0.3 to *ca.* 10 if the H_2SO_4 concentration is changed from 95% to 98%[6,7]. A relatively high $p_{H_2SO_4}$ value leads to effective doping and relatively low p_{H_2O} value minimizes the occurrence of the competing reaction of dopant deactivation by H_2O. The use of H_2SO_4 at concentrations higher than 98% brings about the risk of p_{SO_3} appearance which in turn is an excellent dopant itself but produces films of lower quality.

Figure 2a shows the i.r. spectrum of undoped $(CH)_x$ being a mixture of *cis* and *trans* isomers. Doping of $(CH)_x$ with H_2SO_4 results in a drastic change in its i.r. spectrum (*Figure 2b*). On light doping two new bands ($\nu = 1370\,cm^{-1}$, $\nu = 900\,cm^{-1}$) appear which exhibit remarkable intensity. Their positions are independent of the dopant species[8-10] and only deuteration of polyacetylene can influence them shifting to $\nu =$ *ca.* 1100 and *ca.* 800 cm^{-1} [11]. This shift can be seen in *Figure 2c* and *d* where the spectrum of lightly doped $(CD)_x$ is presented*.

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* Small peaks corresponding to C–H vibrational modes are present in this spectrum due to incomplete deuteration.

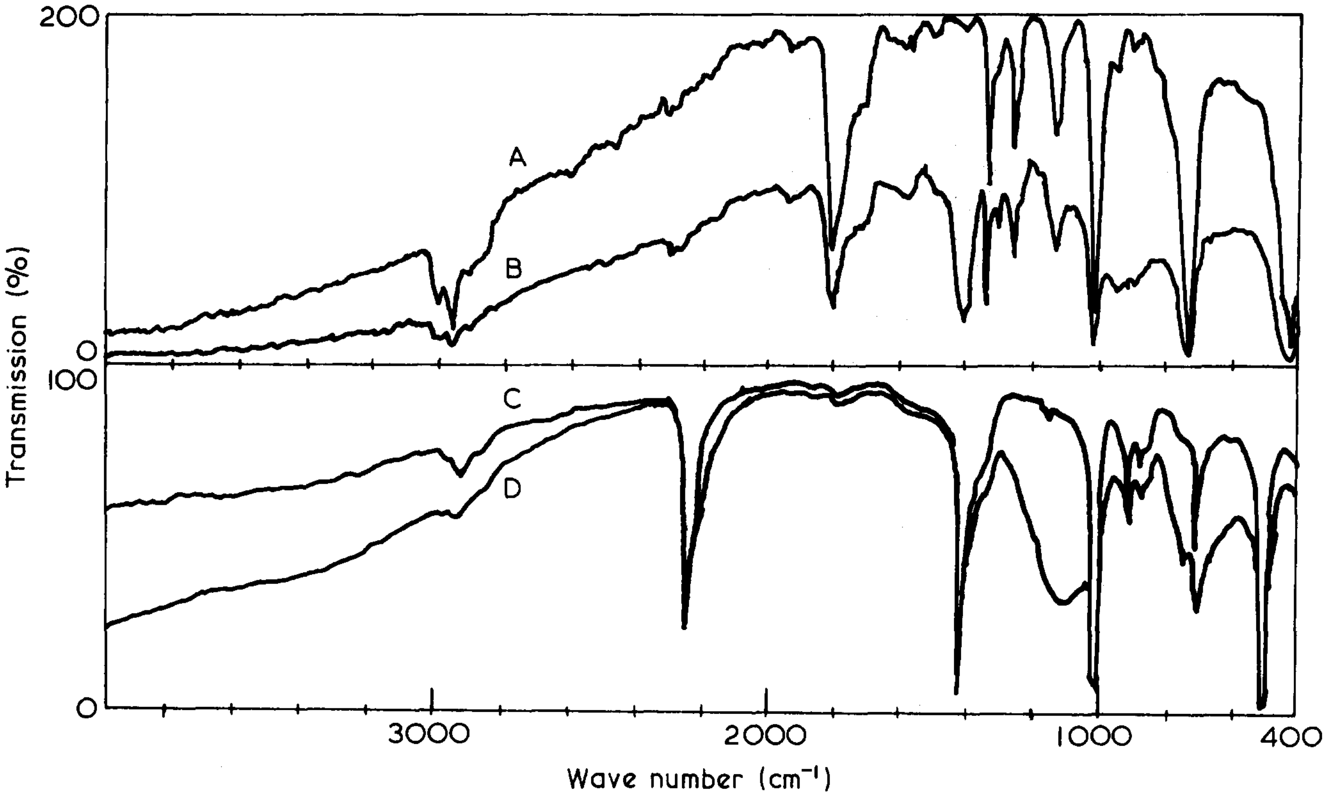


Figure 2 I.r. spectra of undoped and lightly doped $(CH)_x$ and $(CD)_x$: A, undoped $(CH)_x$; B, $(CH)_x$ doped for 2 min; C, undoped $(CD)_x$; D, $(CD)_x$ doped for 2 min

It can be therefore concluded that the new bands are strongly coupled to the polyene chain. Their appearance has been explained[8, 11] by the formation of so called 'charged solitons' and in the subsequent text they will be termed 'soliton bands'.

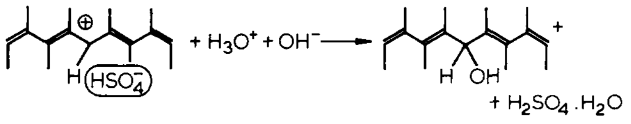
The influence of dry oxygen on i.r. spectra of undoped and lightly doped $(CH)_x$ and $(CD)_x$ are presented in *Figure 3a, b, c*. Oxygen attack causes the formation of two new bands in the stretching deformation region of C=O (ν = 1660 and 1710 cm^{-1}). This assignment is consistent with the spectrum of lightly doped $(CD)_x$ exhibiting large shifts of all existing vibrational modes except the two carbonyl ones. The formation of monoketones and/or diketones can be postulated as being the result of oxygen attack. The existence of a broad weak band between 3300–3600 cm^{-1} for thin $(CH)_x$ films is consistent with the postulation of keto–enol tautomerism or it might also be due to hydroperoxide units. For thick films the existence of this band is obscured by high i.r. absorbtion at high wavelength. Oxygen attack leads therefore to a decrease in conjugation length. Charged solitons are 'trapped' between the defects of the conjugated backbone and the mobility of the carriers decreases.

The reaction of oxygen with undoped $(CD)_x$ leads to essentially the same spectrum as in the case of the reaction of O_2 with the previously H_2SO_4 doped $(CD)_x$ (*Figure 3c*). The formation of 'soliton bands' upon oxygen treatment indicates that oxygen itself can dope $(CH)_x$ concommitantly with the degradation reaction leading to the formation of ketonic defects.

The interaction of deoxygenated water with $(CH)_x$ results in the formation of a weak charge transfer complex as manifested by the appearance of two soliton bands in the i.r. spectrum of $(CD)_x$ treated with H_2O vapours for 17 h (*Figure 4b*). The reaction is reversible since pumping leads to the i.r. spectrum which is practically indistinguishable from the i.r. spectrum of the undoped $(CD)_x$ (compare *Figure 4a* and *4c* spectra).

As was stated previously the reaction of H_2SO_4 doped $(CH)_x$ with deoxygenated water gives a volatile product that can be removed from the film on extended pumping. The above reaction can be classified as a compensation reaction because even when heavily doped, the opaque to i.r. film becomes more and more transmitting after extended treatment with water. This phenomenon is shown in *Figure 5a–d*. The doping and compensation reaction sequence results also in *cis* to *trans* isomerization as can be seen from the relative intensities of the *cis* to *trans* peaks.

It seems highly probable that the compensation reaction results in the formation of hydrated sulphuric acid according to the following reaction scheme:



The formation of carbinol defects upon compensation logically explains the discrepancy between the masses of undoped and compensated $(CH)_x$ (the mass of compensated $(CH)_x$ is consistently higher by *ca.* 10%). High absorption above 3400 cm^{-1} and broad peaks present in the 1450–1350 cm^{-1} and 1100–600 cm^{-1} regions obscure the identification of the -OH functional group, however at 1175 cm^{-1} a weak band can be observed corresponding

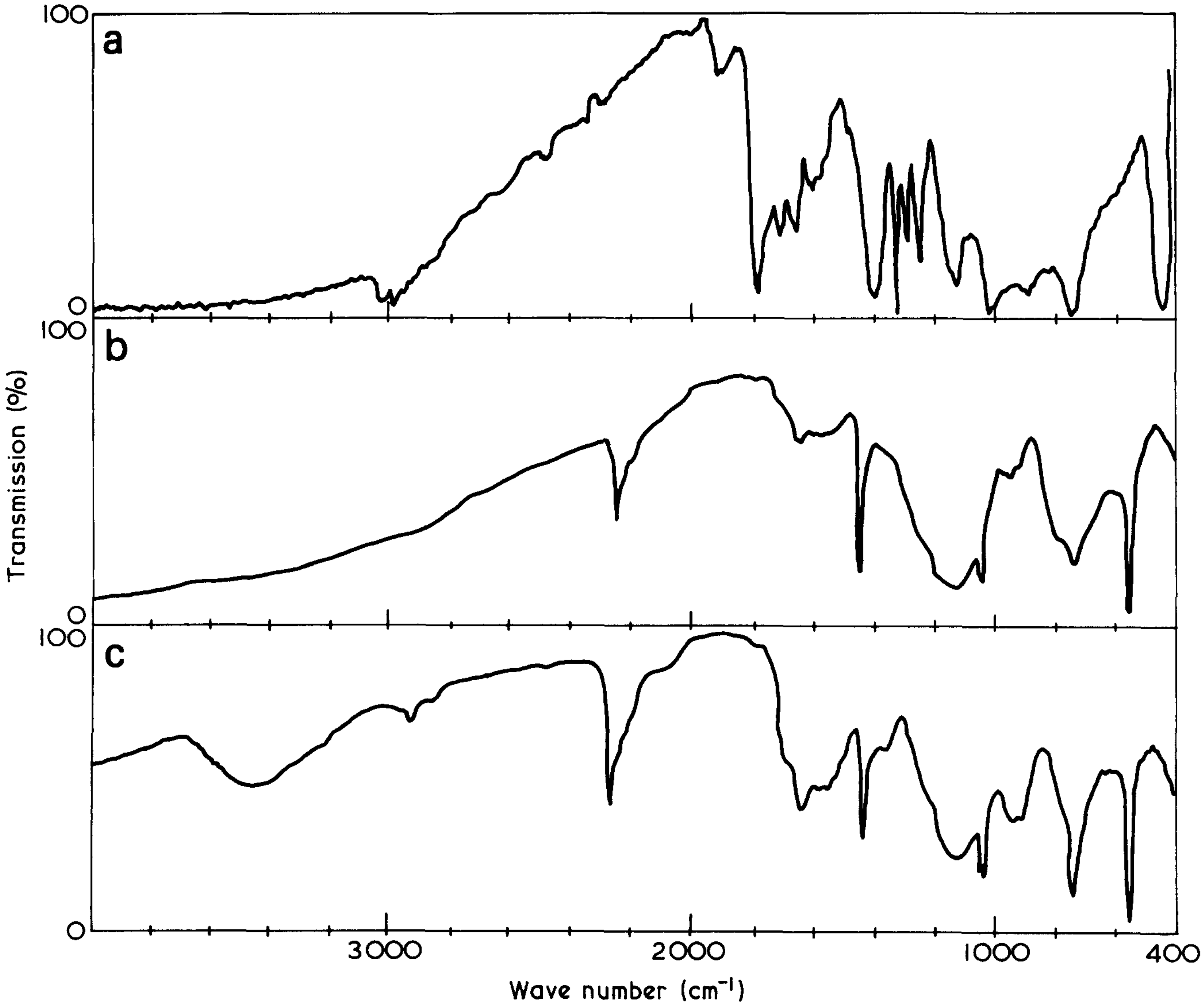


Figure 3 Influence of oxygen on lightly doped $(CH)_x$ and $(CD)_x$ and undoped $(CD)_x$ a, i.r. $(CH)_x$ doped for 2 min; b, $(CD)_x$ doped for 3 min; c, undoped $(CD)_x$

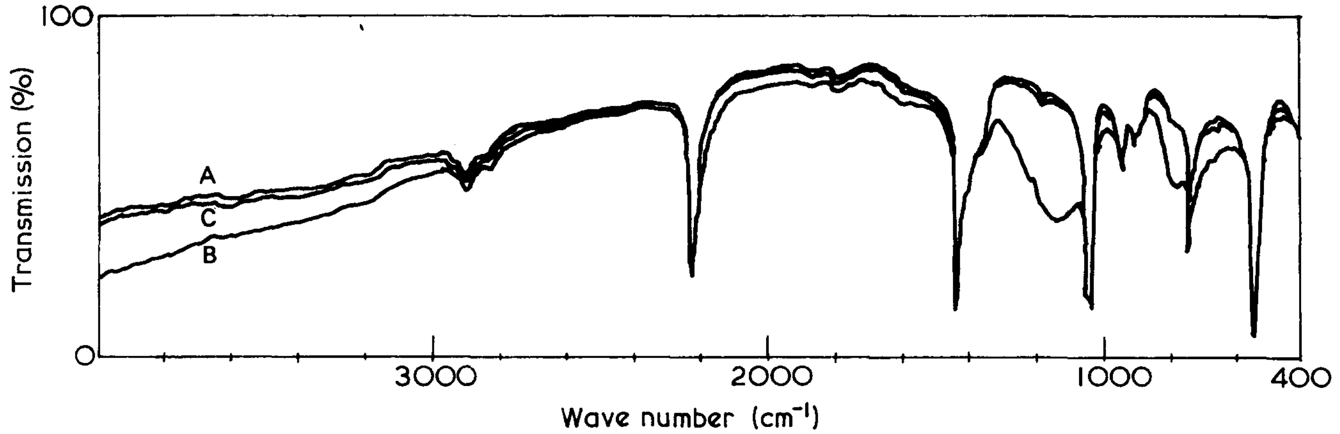


Figure 4 Influence of water on undoped $(CD)_x$: A, Original untreated $(CD)_x$; B, $(CD)_x$ treated with water vapour for 17 h; C, H_2O treated $(CD)_x$ then pumped

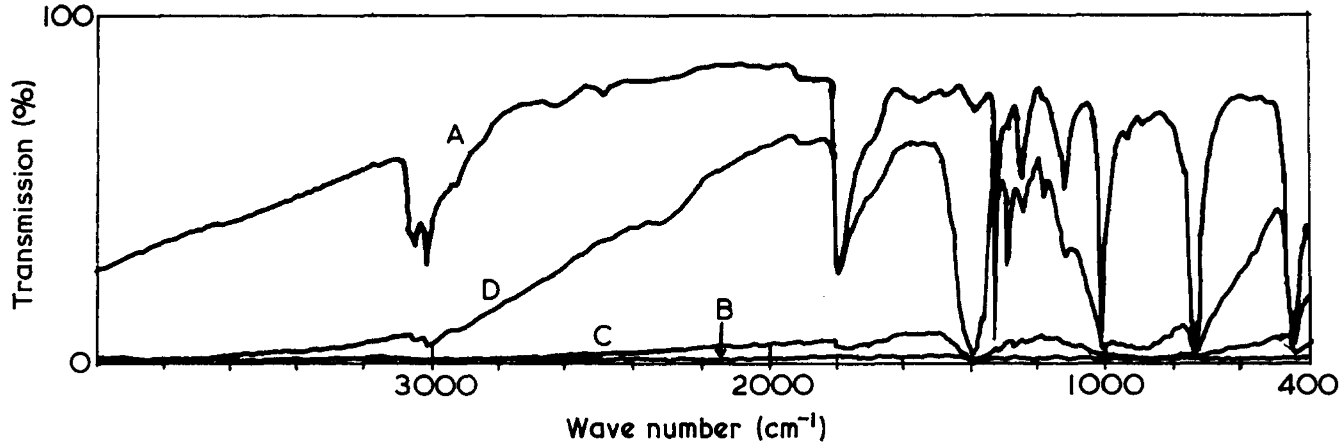


Figure 5 Changes in heavily doped $(CH)_x$ on treatment with water A, original undoped $(CH)_x$; B, opaque heavily doped $[CH(HSO_4)_{0.02}]_x$; C, $[CH(HSO_4)_{0.02}]_x$ washed with water once and pumped; D, $[CH(HSO_4)_{0.2}]_x$ washed with water 11 times and pumped

Table 3 Mass and conductivity changes upon doping, compensation with H_2O and redoping

Reagent	Reaction	τ [h]	No. of water treatments	Δm (mg)	y	z	$[\Omega^{-1}\,cm^{-1}]$	Product
$(CH)_x$	Doping	~3	–	2.77	0.070	–	85.5	$[CH^{+0.07}(HSO_4^-)_{0.07}]_x$
$[CH^{+0.07}(HSO_4^-)_{0.07}]_x$	Compensation	–	10	−2.28	–	~0.070	$<6.6 \cdot 10^{-5}$	$[CH(OH)_{0.07}]_x$
$[CH(OH)_{0.07}]_x$	Doping	~4	–	2.80	0.083	–	170.0	$[CH^{+0.083}(HSO_4^-)_{0.083}]_x$
$[CH^{+0.083}(HSO_4^-)_{0.083}]_x$	Compensation	–	10	−2.70	–	~0.083	$<6.6 \cdot 10^{-5}$	$[CH(OH)_{0.083}]_x$

$m_0 = 5.31$

to the C–O stretching vibration. In addition the amount of OH groups formed on compensation is very low (up to 10%).

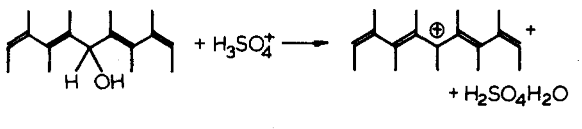
It should be stressed that the existence of hydroxyl groups attached to the chain does not inhibit the doping process. The compensated $(CH)_x$ can be easily redoped with H_2SO_4 to high doping levels. The results of doping, compensation and redoping experiments are summarized in *Table 3*.

The plausible redoping reaction sequence is presented below:

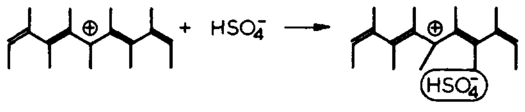
(i) autodissociation of H_2SO_4

$$2H_2SO_4 = HSO_4^- + H_3SO_4^+$$

(ii) oxidation of the chain



(iii) insertion of the counterion



CONCLUSIONS

To summarize the results of this research, it has been unequivocally shown that the correct H_2SO_4/H_2O ratio is crucial for polyacetylene oxidation with sulphuric acid. Gas-phase doping with 98% H_2SO_4 leads to samples of highest quality. The compound obtained exhibits stoichiometry $[CH(HSO_4)_y]_x$ and is unstable with respect to H_2O and O_2. H_2O vapour causes quick compensation of the dopant probably with concommitant formation of polyvinyl carbinol that is dopable. The reaction of doped $(CH)_x$ with oxygen results in the irreversible break in conjugation and an associated slow decrease in conductivity.

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