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Electronic properties of sulfurized polyenes

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Summary :

Relatively short conjugated polyne containing products when treated with sulfur result in materials with low electrical conductivity but with interesting electrochemical activities.

Introduction :

Both thermal and chemical methods have been used in the dehydrochlorination (DHC) of Poly(Vinyl Chloride) PVC to obtain polyacetylene-like properties,i.e., insulating material which becomes highly electronic conducting upon doping with redox compounds (1) . Recently, it was shown that a fully dehyrochlorinated PVC (dhc-PVC) - after thermal treatment with sulfur - leads to materials for batteries of high faradic capacities (2).

In this paper, we will show that the electrochemical properties can be obtained with hybrid systems of sulfur and polymer containing relatively short polyene lenght. The interactions of sulfur with the conjugated polyenes are also discussed.

Experimental :

Materials :

The polymer is a PVC XII of the IUPAC Working Party (3) (Mw = 94500). All others products were used without further purification, except 1,2 dichloroethane (DCE), methanol (MeOH) and

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acetone were distilled before use, THF was distilled in the presence of $LiAlH_4$.

*** Apparatus :**

Spectroscopic studies were carried out using UV-Visible Perkin Elmer 551 or Beckman DU-50 , FTIR Nicolet 20 SX .

The WAXS studies were carried out on powder or pellet of modified PVC (with Cu K_α radiation) at Riken Institute (Japan).

X ray photoelectron spectra was recorded on a Leybold LH ESCA analyser using monochromatized Al K_α radiation (hv = 1486.7 eV). Binding data were refered to Au 4f $_{7/2}$ line (84 eV) of a gold plate fixed on the sample holder.

The electronic conductivity was measured on compacted samples by a Keithley 617 Programmable electrometer according to the conventional four-point probe or two-disc techniques.

The electrochemical properties of the samples were carried out at Laboratory Marcoussis . The preparation of electrochemical cells have been described previously (18). In this study, when ß-carotene was used as electrode materials, the electrolyte Dioxolane/2M $LiClO_4$ was replaced by Propylene Carbonate/1M $LiClO_4$, because of its solubility in Dioxolane.

RESULTS & DISCUSSION :

A. Dehydrochlorination of PVC :

Table I gives the yield of DHC obtained from thermal DHC of PVC in the presence of Zn carbonate ($ZnCO_3$) or triphenyltin monochloride (ϕ_3SnCl), and from the chemical DHC of PVC carried out at moderate temperature using terabutylammonium hydroxide (TBAH) as strong organic base.

The structure of dhc-PVC has been investigated by X rays , the powder WAXS spectrum of PC1 (94 % dhc-PVC) apparently shows that this modified PVC is not fully amorphous. It does not present hump at the Bragg angle of 16°, characteristic of the amorphous phase of polyacetylene PA (4), and it also displays a reflection peak at a Bragg angle of about 23° - almost the same value of cis and trans PA crystals which are in the range of 23 to 25 degrees (5). However, this material cannot be considered as perfect PA crystals (6) since the reflection peak (7) is largely broadened.

TABLE I

Dehydrochlorination of Poly(Vinyl Chloride)

DHC Mode & Solvent	Product Identif.	Temp. °C	Duration Hour	PVC g/l	Nature of Reactant	Conc. g/l	DHC Yield %
Thermal Trichlorobenzene (TCB)	PT1	170	55	2	ϕ_3SnCl + ϕ_2SnCl2	1 4	25
	PT2	170	110	6	ϕ_3SnCl	12	47
	PT3	188	96	5	ϕ_3SnCl	10	52
	PT4	160	24	3.4	ZnCO3	5	24
Chemical	PC1	35	2	7.5	TBAH	55	94
THF	PC2	75	3	6.7	TBAH	38	68

B. Sulfur treatment :

The reaction was at first carried out on a model compound for polyene sequences (ß-carotene). Conditions of reaction and data from the analysis of the products are reported in Table II. It may be observed that limited oxidation takes place even under a stream of nitrogen gas.

At moderate temperature (up to 50°C), there is pratically no interaction. Strong interaction takes place at a temperature above 150°C ; IRTF studies show a new sharp band at 667 cm-1 after about 30 minutes at 175°C .This band may be assigned as the stretching band of a covalent C-S bond, expected to be located in the range 625-715 cm-1 (9). It can be considered as an evidence for the grafting of sulfur. Such reaction gives rise to the formation of H_2S and causes the H/C ratio to drop sharply (about 30% of the ethylenic hydrogen atoms have been lost) (sample ßS3 in Table II) . This interaction does not saturate all the double bonds however, because in the IR spectra the rather strong band near 1620 cm^{-1} still remains. Nevertheless, the structure of the double bonds have been modified : a relative decrease of the two bands at 3014-3028 and 957 cm^{-1}, which are characteristic of the ethylenic vibration (stretching *trans* structure and out of plane *trans* deformation respectively) is observed.

TABLE II

Sulfur Treatment of ß-Carotene (Atomic Ratio S/C =1)

Product	Solvent	Gas Stream	T°C	React. Time Hours	Product Analysis		
					H/C	S/C	O/C
ßS1	DCE	N2	75	2	1.1	0.89	0.016
ßS2	DCE		75	2	1.18	0.93	0.04
ßS3*	THF	N2	65	3	0.58	0.58	0.06

The presence of C-S bond has been also checked by ESCA. The ESCA spectrum of ß-carotene (Fig. 1a) presents an asymetric main peak located at 285 eV with full width at half maximum (FWHM) of 2.1 eV. The decomposition of this line into a Gaussian-Lorentzian line shape components gives rise to two peaks located respectively at 284.9 and 286.6 eV showing partial oxidation of the sample surface. Within experimental error, there is no observable shift of the peak position of the C 1s line in the doped sample. However, as shown in Figure 1b, upon doping the line is broadened (FWHM = 2.6 eV) indicating the formation of new chemical sites . Therefore the new peak at 285.6 eV in the resolved curve of the spectrum could be assigned to C-S bond in the doped sample (4). Furthermore, it is noteworthy that different types of sulfur atoms - such as those involved in the charge tranfer complex - would be present in the doped sample because the 2 :1 doublet due to spin orbit splitting of the S 2p level in single environment is not observed as shown in the S 2p

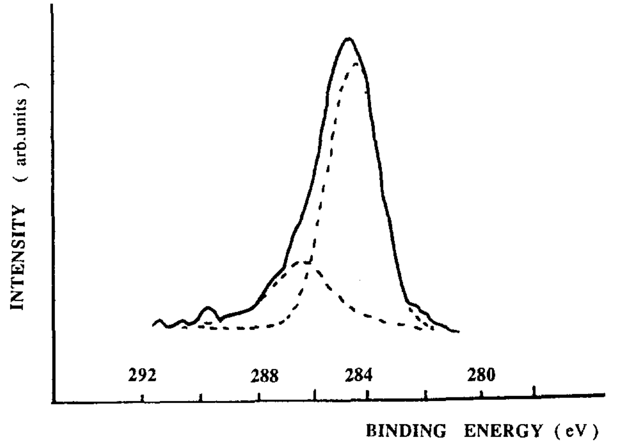

Fig.1a : C 1S spectrum of pristine ß-carotene .

spectrum with its decomposition into S 2p 1/2 and S 2p 3/2 (5,6) (Fig. 1c).

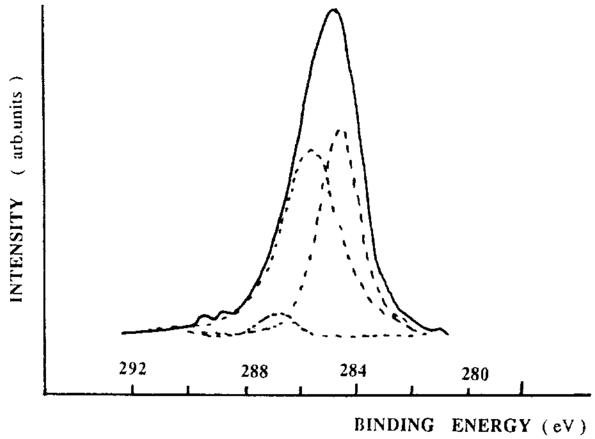

Fig.1b : C 1S spectrum of Sulfur-doped ß-carotene

The heat treatment of dhc-PVC, with sulfur in various conditions are reported in Table III. The interaction of sulfur with dhc-PVC is very similar to that observed with ß-carotene. In fact, the infrared spectra show that double bonds still exist and that grafting of sulfur may be detected when the amount of sulfur implied is large enough (S/C= 1.45) . In this case some free sulfur remain as evidenced by the strong band at 461 cm^{-1}. The loss of hydrogen, as well as of sulfur, is also observed. in these cases (samples PT1S, PT2S, PT3S) due to the formation of H_2S. When the starting products were oxidized (PT2, PT3) most of oxygen remain in the samples after sulfuration. However the carbonyl band around 1720 cm^{-1} is broader and shifted to lower wavenumber. This could be arised from the interaction of sulfur with the conjugated double bonds .

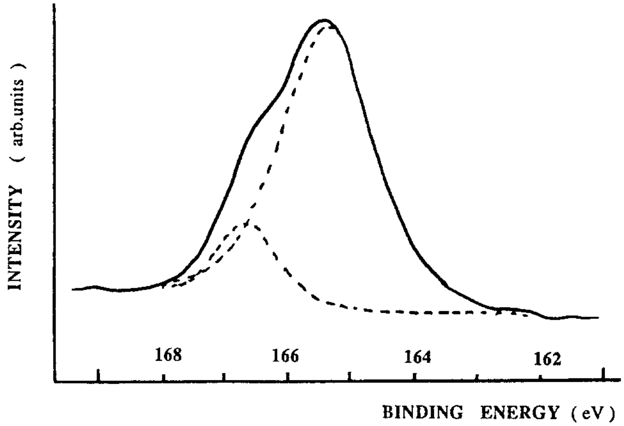

Fig.1c : S 2p spectrum of Sulfur-doped ß-carotene and resolved components.

TABLE III

Doping of Dehydrochlorinated PVC with Sulfur

Sample	Initial S/C ratio	Solv.	Heat T°C	Treatment Time Minutes	Final S/C ratio	Product Analysis O/C	H/C
PT1S	1.4	TCB	175	240	0.12	?	0.75
PT2S	1.4	DCE	180	75	0.73	0.372	0.53
PT3S	2.5	MeOH	65	65	1.45	0.412	0.8
PT4S	0.73	DCE	75	180	0.14	?	2.4
PC1S	1.3	THF	65	360	1.08	0.07	1.13
PC2S	1.94	THF	75	270	1.36	0.078	1.5

C. Electrical and Electrochemical properties :

The electric conductivity of dhc-PVC is rather low (from 10^{-9} S/cm when the DHC yield was 50%) to 10^{-8} S/cm (for a DHC yield of 94%). Upon doping with Iodine, the conductivity increases only from 10^{-9} to 10^{-6} S/cm. This is far from the high values up to $2x10^{4}$ S/cm (11) recently reported for high oriented polyacetylen samples of very long conjugated polyene chain. The poor conductivity of our samples can be explained by the very low cristallinity of dhc-PVC as evidenced by the WAXS spectra and the short length of polyene sequences obtained in the experimental conditions .

When doped with sulfur, no increase in conductivity have been observed for dhc-PVC or ß-carotene and although the sulfurated samples have low conductivities, as indicated in Table IV, they display interesting faradic capacity once they are used as electrode materials. The discharge curves of standard button cells of Li/ßS3 , Li/PT2S , Li/PC1S and Li/PT3S are shown in Fig.2. Furthermore, the result obtained using the ßS3 sample shows that the presence of very long polyene sequences is not mandatory to observe the electrochemical activity : the number of double bonds in the chains is not greater than 11 and might be lower if some saturation process had taken place. So, it appears that any DHC method that can give 50% dehydrochlorination PVC, followed by a heat treatment with sulfur, can be considered

TABLE IV

Electronic and Electrochemical Properties of Sulfur - Conjugated Polyenes Materials

Product symbol	Faradic Capacity Ah/kg	Voltage V	Electronic Conductivity
PT2S	280	2.1	$< 10^{-9}$ S/cm
PT3S	800	2.1	$< 10^{-9}$ "
PC1S	700	2.1	$= 10^{-6}$ "
ßS3	200	2.2	$< 10^{-9}$ "

available to produce electrochemically active material. In fact, the absence of faradic capacity is observed for samples with a DHC yield limited to ca 25% (PT1 and PT4). On the other hand,the best result comes from PCS1 starting from PC1 with a DHC yield of 94%, while the other chemically degraded sample PCS2 is not active, probably due to the interchain crosslinking reaction taking place at higher temperature .

Finally, if the faradic capacity is due to the charge transfer complexes between sulfur and/or polysulfur and the conjugated double bonds (2), it might also be expected to be linked to the grafted

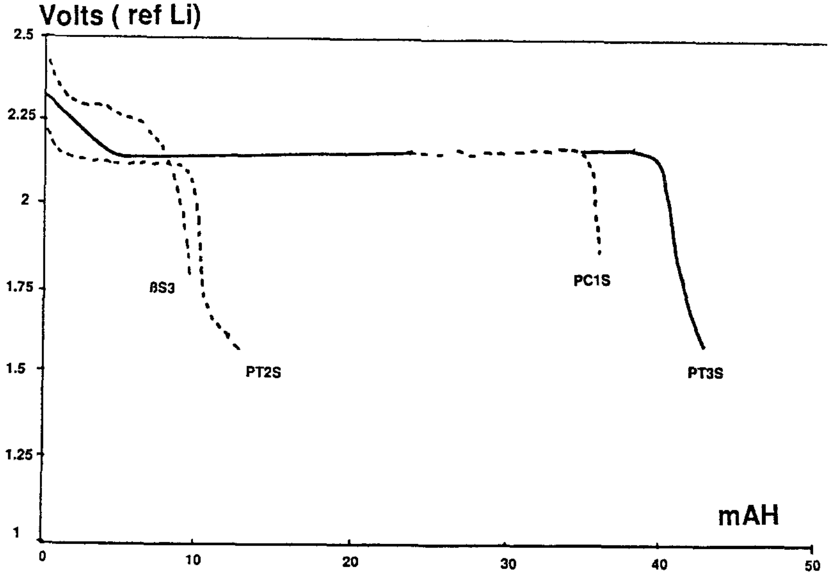

Fig. 2 : Discharge curves of standard button cells:

ßS3 (LI/ßS3) ; PT2S (Li/PT2S) ; PC1S (Li/PC1S) ; PT3S (Li/PT3S) sulfur of the covalent bond C-S as well as to the free sulfur in the polymer matrix; the arguments are that the sulfur doped dhc-PCV (or ß-carotène) did not show any improvement in electrical conductivity and that neither the presence of C-S bonds nor of oxygen containing structures inhibit the developpment of the faradic capacity (PC1S, PT2S and PT3S), and finally that a high enough amount of sulfur must be used. It is noteworthy that the sulfur fixed on carbon atom has almost the same electrochemical behavior as the elemental sulfur (10).

CONCLUSION :

Any dhc-PVC of relatively short conjugated polyene sequences (ca 11 double bonds) obtained by DHC of PVC can be used as material electrode after treatment with sulfur . On the basis of our results, the faradic capacity and the air stability of the sulfurised DHC-PCV are expected to come not only from the charge transfer complex between free sulfur and conjugugated polyene sequences (2), but also from the sulfur either free or grafted onto the polymer matrix.

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