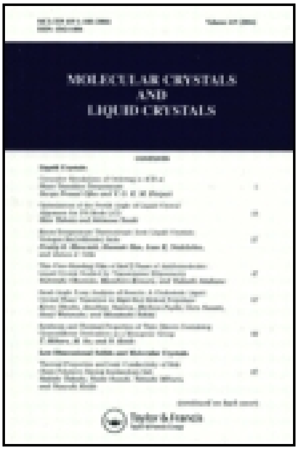

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N Doping of Polyaceiylene by Carbarionic Salts and Alkyllitnium Compounds

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N DOPING OF POLYACETYLENE BY CARBANIONIC SALTS AND ALKYLLITHIUM COMPOUNDS.

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Abstract : PA was doped by organolithium compounds in polar and non polar medium. A large range of doping rate is observed. The max. conductivity is correlated to the redox potential of dopants. New data on the influence of cation solvation are reported.

The first chemical N dopings of Polyacetylene (PA) were carried out by reaction with alkaline metals, their alloys or amalgames, or their salts of radical-ions (naphtalene Na) (1).

We shown that alkali dianionic complexes of aromatic ketone (benzophenone) (2) and carbanionic salts(3) are also effective dopants. Some characteristics of a new class of dopants (alkyl lithiums) able to dope PA in non polar solvent, are now reported. A correlation is established between the redox potential of some N dopants and the maximum electrical conductivity available with these dopants.

SYNTHESIS OF PA FILMS

PA films (100 microns thick) are prepared by a modified Shirakawa technique. A control of pressure and flow of the monomer allows the formation of highly porous films without the shiny surface acting as a barrier for dopant diffusion (4). The diffusion coefficient of n-dodecane (mean size of dopant molecules) through the films immerged in THF was determined: a typical value of 7.10^{-6} cm^2/sec was measured for thickness of films ranging from 50 to 1500 microns. The interfibrillar diffusion time is then short compared with the doping time. The cis-trans isomerization is carried out at 180° and the conductivity of pure cis and trans PA are typically 10^{-12} and 10^{-9} S/cm.

KINETICS OF DOPING BY ALKYLLITHIUMS AND LI CARBANIONIC SALTS.

All dopings are carried out in sealed glass apparatus (5) and the electrical conductivity is measured as a function of the doping time (Fig 1). The corresponding experimental conditions as well as the maximum doping levels and maximum conductivity are collected in Table 1. The doping level, y, was determined by *chemical analysis of Li. The observed weight increase during the* doping is in excess towards the y value. A large range of doping rate is observed in non polar solvents: concentrated n Butyllithium (nBuli) in hexane leads slowly to high doping level. This rather unique property is favorable to an homogeneous doping process. The s Buli is more reactive than n Buli and the reactivity of both isomers is increased by addition of complexing agents such as Tetramethylethylene diamine (TMEDA). Diphenylhexyllithium (DPHLi) is much more efficient than Buli even at lower concentrations. The results are similar in cyclohexane and in diethylether: No variation of conductivity is observed after cryogenic pumping of $(CHLi_{0.19})_x$ doped in ether while an increase by a factor 37 is observed for doping in THF. According to our previous explanation (3) this means that THF strongly solvates Li^+ while ether does not. Finally it is observed that an increase of doping temperature increases the doping rate but not the max. conductivity.

REDOX POTENTIAL OF N DOPANTS AND MAX.CONDUCTIVITY

As the redox potential of N doped PA decreases with its doping level (6) the maximum doping level possible with a given electrodonor depends on its redox potential. The doping reaction stops when both redox potentials are equivalent. While strong *dopant such as naphtalene sodium leads practically to the highest* possible dopings, carbanionic salts cover a large range of potential allowing a partial doping or no doping at all. We report here the max.cond. for cis and trans PA doped with 0.1M solutions in THF of naphtalene radical-ion (N), benzophenone dianion (B), diphenylmethyl (DPM), triphenylmethyl (TPM), fluorenyl (F) and indenyl (I) carbanions.

Redox potentials of these compounds are deduced from litterature data (7,8).

Indenyl Li lightly dopes cis PA (confirmed by ESR) but not the trans isomer. Indenyl Na has no effect in any case.

From these data the redox potential of pristine PA is estimated at -0.6 V (ref: $H2/H+$).

SOLVENT EFFECTS IN HIGHLY DOPED CHLi

Doping in polar solvent is complicated by solvent effects on conductivity and swelling (3). At low doping level it was shown that solvation of cations by THF increases the conductivity while at high doping level the contrary was observed. We studied the influence of THF vapor pressure on the swelling (variation of length: fig 3) and on the conductivity of $(CHLi_{0.1})_x$ (fig 4). From the fig 5, obtained by combination of fig 3 and 4, it can be seen that the major part of the conductivity variation occurs with a weak length variation. That could mean that the solvent effect is essentialy due to solvation near the fiber surface.

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Table 1 : Experimental conditions for fig 1

Exp.	Dopant	Conc.	Solvent	Temp.	max	y max
1	n Buli	1.5 M	Hexane	25°	20	.11
2	s Buli	1.4	cyclohex.	25°	143	.15
3	"	1	benzene	25°	116	.19
4	"	1.4	cyclohex.	80°	99[a]	
5	n Buli/TMEDA	1.2	hexane	25°	>49	
6	s Buli/TMEDA	1	cyclohex.	25°	90	.23
7	DPHLi	.03	"	25°	167	.24
8	"	sat.	"	70°	152[a]	
9	"	.5	ether	25°	173(175[b])	.19
10	DDLi2[c]	.2	THF	25°	21(766[b])	
11	PhenylLi	.05	benz/ether	25°		

a : value measured at temperature of the experiment
b : " " after cryogenic pumping
c : Tetraphenyl 1,1,4,4 butylene dilithium

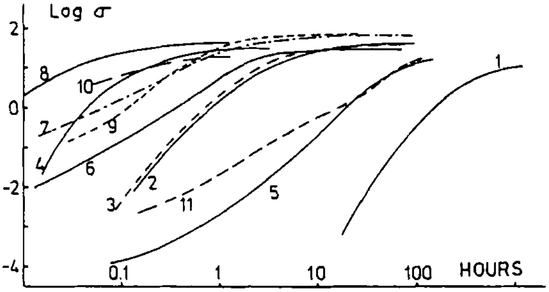

Fig.1 : d.c. conductivity of N doped PA as a fonction of doping time (- conditions in table 1 -)

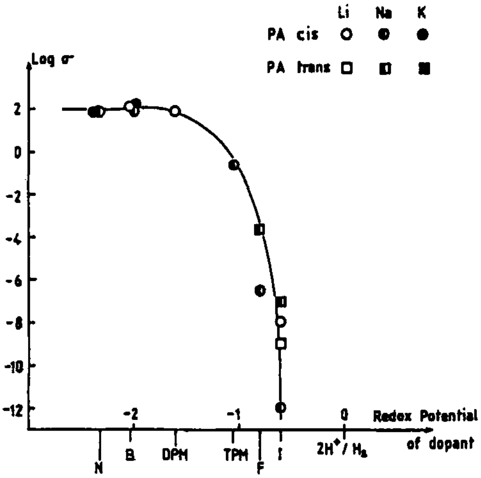

Fig.2 :
max. d.c. conductivity of N doped PA versus redox potential of N dopants (0.1M) in THF

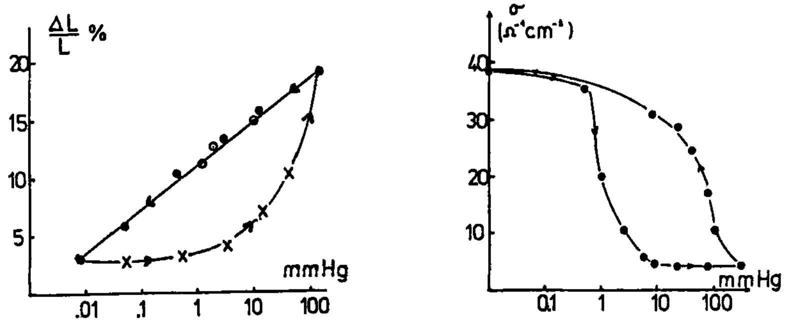

Fig.3 and 4 : length and conductivity variations of $(CHLi_{0.1})_x$ versus THF vapor pressure : evidence for hysteresis phenomenon

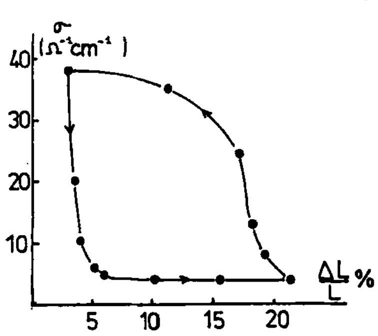

Fig.5 :
d.c. conductivity of $(CHLi_{0.1})_x$ in THF vapor versus length increase