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The correlation between electrical properties and structure of substituted polyacetylenes

A. Janevski*, S. Leben, A. Šebenik, and U. Osredkar**

Boris Kidrič Institute of Chemistry, Ljubljana, Yugoslavia

SUMMARY

The electrical conductivity of polyphenylacetylenes and polyhalophenylacetylenes was measured in dependence on the temperature and on the type of catalyst used for polymerization. The electrical conductivity increased with increasing temperature. The energy gap was calculated from the temperature dependence on the electrical conductivity; it decreased with increasing number of conjugated double bonds in the polymer chain and with the regularity of structure of the polymer. The number of double bonds, cyclization and configurations were determined by ^1H and ^{13}C-NMR. In polyphenylacetylenes only aliphatic carbons deriving from cyclohexadiene units were found, but no such units were found in polyhalophenylacetylenes. By UV-vis measurement the number of conjugated double bonds in segments was estimated. The synthesized polymers were amorphous. Their molecular weight was between 2000 and 74.000.

INTRODUCTION

The electrical properties of conductive polymers depend on many factors, mostly on conjugation and on crystallinity. The energy barrier (gap) consists of the energy of transition of electrons in the polymer chain and of the energy of electrons motion from chain to chain. The first depends on the energy differences of orbitals of the valent and conductive bands, while the second depends on the configuration of the chains and their packing in crystal (1). Only polymers with sterically regulated side groups and chain configuration can crystallize, but most of them have random configurations and therefore are amorphous materials.

In this work the influence of phenyl and halogen substitution of polyacetylenes on the polymer properties, on the energy gap and on the conductivity using UV-vis, NMR, X-ray and conductivity measurement were investigated.

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*Permanent address: OHIS Skopje, Yugoslavia

**To whom offprint requests should be sent

EXPERIMENTAL

Materials: Phenylacetylene was a product of Merck. All reagents used in this work were of p.a. grade. Halophenylacetylenes were synthesized using butyllithium and corresponding halogenes as reagents (2).

Polymerization: Polyphenylacetylenes (PPA 1-3), polychlorophenylacetylene (PClPA) ,polybromophenylacetylene (PBrPA) and polyiodophenylacetylene (PIPA) were synthesized with coordination catalysts $Ti(OBu)_4$-$Al(Et)_3$, $MoCl_5$-Ph_4Sn and WCl_6-Ph_4Sn. Dry CCl_4 and toluene in argon atmosphere were used as solvents. After polymerization the polymers were precipitated twice from CCl_4 using methanolic solutions of HCl (3-7). All polymerization parameters and properties of the polymers are given in Table 1.

Measurements: Molecular weight distribution of polymers was measured using a Perkin Elmer GPC with PL columns with pore size $1 \cdot 10^{-8}$ and $5 \cdot 10^{-8}$m.THF was used as solvent. The polystyrene standards were used for columns calibration. X-ray diffractograms were recorded on a Philips PV-1710 Cu-Kα diffractometer. NMR spectra were recorded using a Varian supraconducting 300 MHz spectrometer.$CDCl_3$ was used as solvent; all signals are given on the TMS as reference standard. UV-vis spectra were recorded in CCl_4 using a Varian spectrometer. For electrical measurements the samples were pressed in pellets. The measurements were run in dry argon atmosphere in the temperature range between 294 and 400 K.

RESULTS AND DISCUSSION

The average molecular weights of the substituted polyacetylenes are between 22000 and 74000 for polyphenylacetylenes and between 2000 and 25000 for polyhalophenylacetylenes (Table 1).

The influence of the increasing size of halogen atoms on the decreasing of the molecular weight is evident and is due to sterical hindrances of halogen on the coordinative catalyst system.

The amount of olefinic and aliphatic carbons in the substituted polyacetylenes was measured by ^{1}H and ^{13}C-NMR using the method of Perces and Rinaldi (8,9). The results are given in Table 2.

The polymers are mostly in trans configuration. In all polyphenylacetylene samples some cyclohexadiene units were found. Their quantity depends on the polymerization conditions and on the type of catalyst. There were no cyclohexadiene units in polyhalophenylacetylenes. No signals of other aliphatic $-\overset{|}{\underset{|}{C}}H$ or $-\overset{|}{\underset{|}{C}}-$ groups were found. From the amount of cyclohexadiene units in the polymer chains, the ratio between the double and single bonds was calculated. The ratios are given in Table 2. Due to the sterical hindrances of the side groups and to nonplanar chain configuration, the number of conjugated double bonds in the individual polymer segments is equal or smaller

Table 1. Polymerization parameters of polyphenylacetylenes and polyhalophenylacetylenes with different catalyst systems

Type of polymer	Catalyst	Polym.time (h)	Polym.temp. (°C)	Yeald (%)	Molecular weight	n*	Colour
Polyphenylacetylene (PPA-1)	$Ti(OBu)_4$-$Al(Et)_3$	0.5	20	43.4	28 622	194	ocher
Polyphenylacetylene (PPA-2)	$MoCl_5$-Ph_4Sn	24.0	45	63.0	74 045	514	yellow
Polyphenylacetylene (PPA-3)	WCl_6-Ph_4Sn	1.0	20	80.6	22 160	151	red
Polychlorophenylacetylene (PClPA)	$MoCl_5$-Ph_4Sn	48.0	60	36.6	24 933	181	yellow
Polybromophenylacetylene (PBrPA)	$MoCl_5$-Ph_4Sn	18.0	70	4.4	14.274	104	brown
Polyiodophenylacetylene (PIPA)	$MoCl_5$-Ph_4Sn	18.0	70	13.9	1 819	9	black brown

*n average number of monomer units in polymer

Table 2. The properties of polyacetylene, polyphenylacetylenes and polyhalophenylacetylenes

Type of polymer	λ_{max} (nm)	$\lambda_{\epsilon=0}$ (nm)	($\Delta 2\theta/2\theta$)	Energy gap (eV)	Conductivity ($\Omega^{-1}cm^{-1}$)	Cyclohexadien units (%)	Trans units (%)	Cis units (%)	Ratio of double and single bonds
PA (12)	700	>800	<0,20	0,49	$7,1.10^{-5}$	/	96.0	4.0	/
PPA-1	313*	477	0,43	1,4	$1,5.10^{-15}$	30.0	64.0	6.0	0.5 : 1
PPA-2	329	492	0,41	1,2	$6,0.10^{-16}$	12.3	71.3	16.4	3.0 : 1
PPA-3	336	572	0,41	1,0	$2,8.10^{-14}$	16.8	83.2	0.0	5.0 : 1
PClPA	310	385	/	1,4	$2,0.10^{-16}$	/	/	/	/
PBrPA	301*	551	0,55	1,4	$5,2.10^{-16}$	/	/	/	/
PIPA	306*	600	0,50	1,3	$1,3.10^{-15}$	/	/	/	/

*estimated by the deconvolution method

than the number of double bonds. The relation between the number of conjugated double bonds and UV-vis absorption (10), was confirmed. With increasing number of conjugated double bonds the lowest energy $\pi \rightarrow \pi^*$ transition is shifted to higher

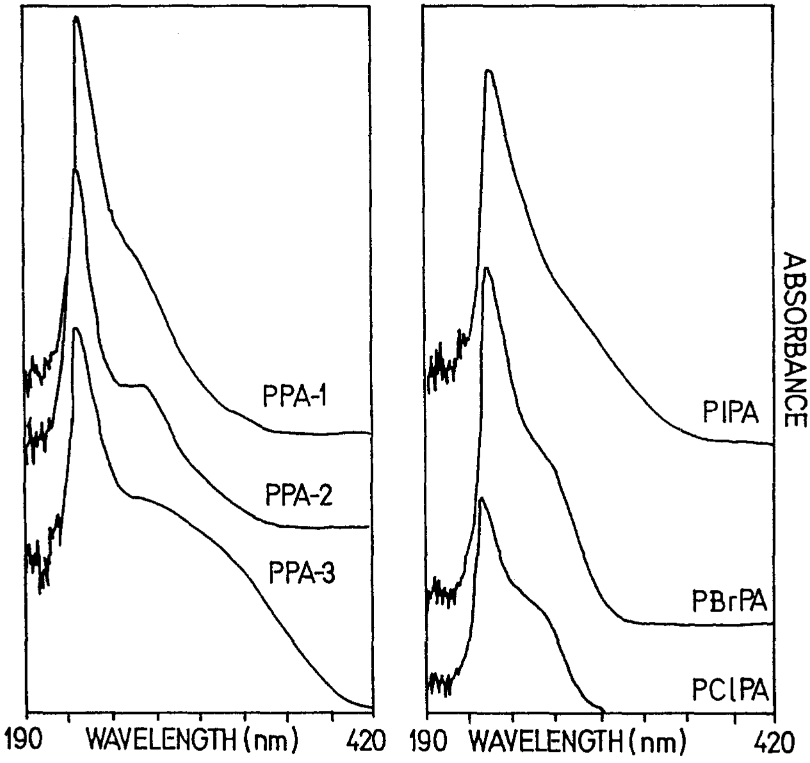

Figure 1. UV-vis spectra of polyphenylacetylenes and polyhalophenylacetylenes

wavelength values. In Fig. 1 the UV-vis spectra of polyphenylacetylenes and of polyhalophenylacetylenes while in Table 2 the λ_{max} and $\lambda_{\epsilon=0}$ (UV-vis cut off) values are given. For PPA-3 with WCl_6-Ph_4Sn as catalyst, the conjugation was the highest and the broad signal of $\pi \rightarrow \pi^*$ transition shifted to 572 nm. Between the PPA samples the lowest conjugation was found in PPA-1 with the highest content of cyclohexadiene units which breaks conjugations of the double bonds in the chain. Between PPA-2 and PPA-3 there is a discrepance in the ratios of double and single bonds and the conjugation. From the literature (8,9) it is known that, when PPA is synthesized with wolfram catalyst, trans structure is produced only. Under the selected conditions for polymerizations of PPA-2 16.4% of cis isomer was formed. The lower conjugation in PPA-2 as compared to the conjugation of PPA-3 is, probably, due to steric repulsions between the phenyl groups and the hydrogen atoms.

Due to smaller number of conjugated double bonds in the segments UV-vis absorption maxima of polyhalophenylacetylenes are at a lower wavelength values as compared to PPA samples. The halogen atoms cause additional sterical hindrances, which twist the chain to non planar configuration.As a result the wavelength of $\pi \to \pi^*$ transition is shifted to lower values.

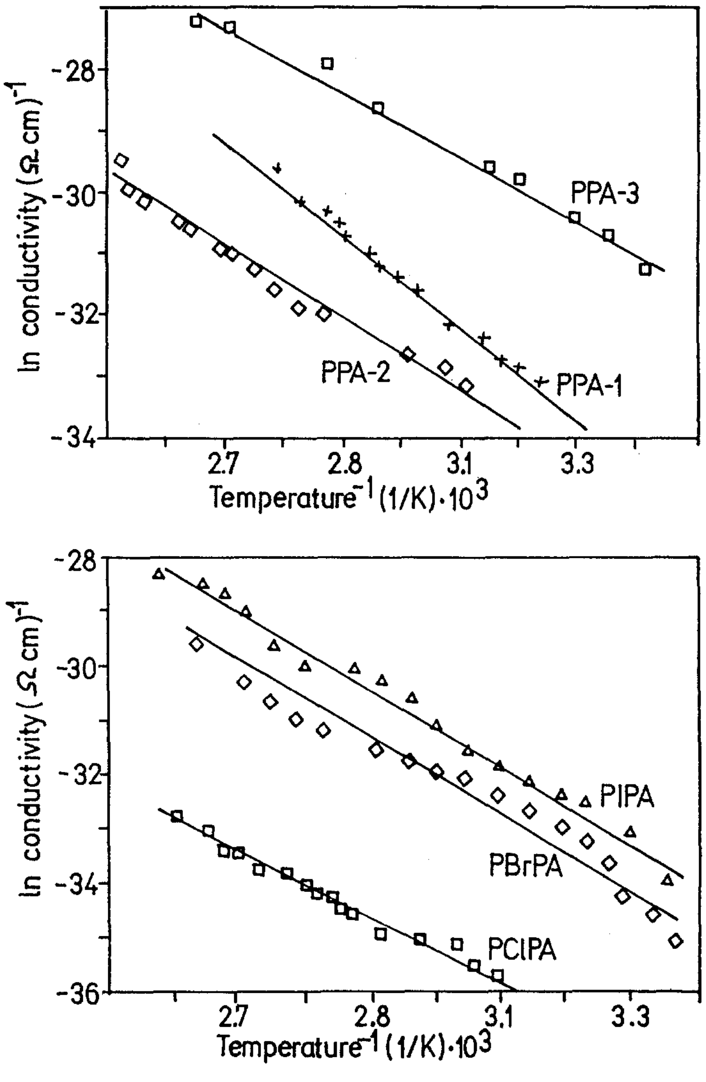

Figure 2. Dependence of the electrical conductivity on the inverse temperature for polyphenylacetylenes and polyhalophenylacetylenes

The regularity in structure for all investigated samples in solid state was measured by X-ray diffraction. Materials with $\Delta 2\Theta / 2\Theta < 0.2$ are crystals, ($\Delta 2\Theta$ is the width of the peak on half height and 2Θ is the diffraction angle) (11). It was found that all our samples were amorphous (Tab. 2). The crystallinity of PPA is prevented by the presence of cyclohexadiene units and of both isomers (cis-trans) in the polymers. Due to the halogen atoms and to the phenyl side groups, which sterically prevent the formation of regular planar or helical chain conformations and thus the crystallization of polymers, the polyhalophenylacetylenes are even more disordered.

All these effects contribute to the electrical conductivity and to the energy gap. Since the electrical conductivity increases with increasing temperature all investigated samples can be classificated as semiconductors.

The energy gaps of the synthesized polymers were calculated from the dependence of the conductivity on the temperature (Fig. 2), using equation

$$\sigma=\sigma_o e^{-Eg/2kT}$$

where σ represents the conductivity at a given temperature.

The slope of the straight line in the diagram $\ln\sigma$ versus $1/T\ 10^3$ corresponds to the $E_g/2k$. The calculated E_g and conductivities of individual polymers are given in Table 2. The lowest E_g has PPA-3, which has the highest conjugation in the chain and some regularity in the polymer structure as compared to other samples.At the same time PPA-3 has the highest conductivity.

Compared to polyacetylene , the energy gaps of the substituted polyacetylenes are higher and conductivities lower, due to smaller conjugation in the polymer chain and to amorphous structure, although it was expected that resonate and charge contribution of the benzene rings and of the halogen atoms should decrease E_g and increase the conductivity.

CONCLUSIONS

The electrical properties of the substituted polyacetylenes depend on the conjugation and on the regularity in polymer structure.

The conjugation is lower as compared to polyacetylene, due to cyclohexadiene units, configurations and large substituents. The structure was amorphous. Therefore, the energy gaps were higher and the conductivity lower as compared to polyacetylene.

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