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Characterization and Doping of Poly(Paraphenylene) Prepared By Catalyzed Electropolymerization

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CHARACTERIZATION AND DOPING OF POLY(PARAPHENYLENE)
PREPARED BY CATALYZED ELECTROPOLYMERIZATION

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Abstract A new poly(paraphenylene) recently obtained by electropolymerization of dihalobenzene is described in terms of infra-red and UV-visible absorptions, electron paramagnetic resonance, DC conductivity of the pristine material. The first data on AsF_5 doping are given. The properties of the electropolymer are compared to those of other poly(paraphenylene) synthesized by chemical methods.

INTRODUCTION

For the last few years, poly(paraphenylene) PPP has been mainly synthesized by two methods¹⁻². The resulting polymers are different owing to the different chemical nature of the growing species involved in the polymerization reactions³. It is well known that PPP is an electroactive polymer⁴⁻⁵ whose transport properties are influenced by impurities⁶, and thus the synthesis method determines in part the polymer behavior. In this paper, we report briefly on a new PPP, obtained by electropolymerization⁷ of dihalobenzene, which show some interesting peculiarities.

ELECTROPOLYMERIZATION

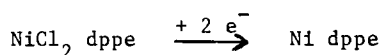
The electropolymerization was carried out under argon at room temperature in a three electrode cell with cathodic and anodic compartments separated by a sintered glass disk. The working electrode was a mercury pool and lithium was used as the counter

electrode. The potential of the working electrode against a Ag/AgClO_4 0.1 M reference electrode was fixed by a SOLEA-TACUSSEL potentiostat at - 2.6 volts.

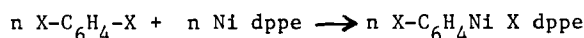
The electrolyte was obtained by dissolving LiClO_4 in a mixture of THF-HMPA⁷. The monomer was either paradibromobenzene or paradibromobiphenyl and the reaction was catalyzed by a complex $\text{NiCl}_2(\text{C}_6\text{H}_5)_2\text{P}-\text{CH}_2-\text{CH}_2-\text{P}(\text{C}_6\text{H}_5)_2$ (NiCl_2 dppe).

The reaction followed the general scheme :

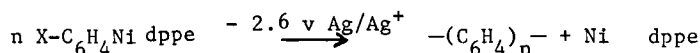
- generation of zero valent Nickel complex by electroreduction



then



- reduction of the above complex leading to polymerization



After the electrolysis, the yellow suspension was acidified and the solid was filtered out. It was then thoroughly washed with various solvents and treated with boiling solutions of HCl 2 M. The remaining yellow polymer was finally dried under vacuum after further washing with solvents (yield close to 80 %). Elemental analysis showed that the polymers contained about 4 % of bromine.

CHARACTERIZATION

FTIR

The infra-red spectra of the electropolymers showed the same features as the regular PPP : standard vibrations at 1000, 805.5-806 ; 764-766 and 691-694 cm^{-1} . In figure 1, we have represented the 650-900 cm^{-1} region taken from a typical spectrum. The vibrations taking place in this range allowed an estimate of the mean chain length as it is well known that the CH out of plane vibration for a para disubstituted benzene ring (around 800 cm^{-1}) shifts toward

lower frequencies as the chain length increases. The opposite behavior is observed for the CH out of plane vibration for a mono substituted benzene ring (around 760 cm^{-1}).

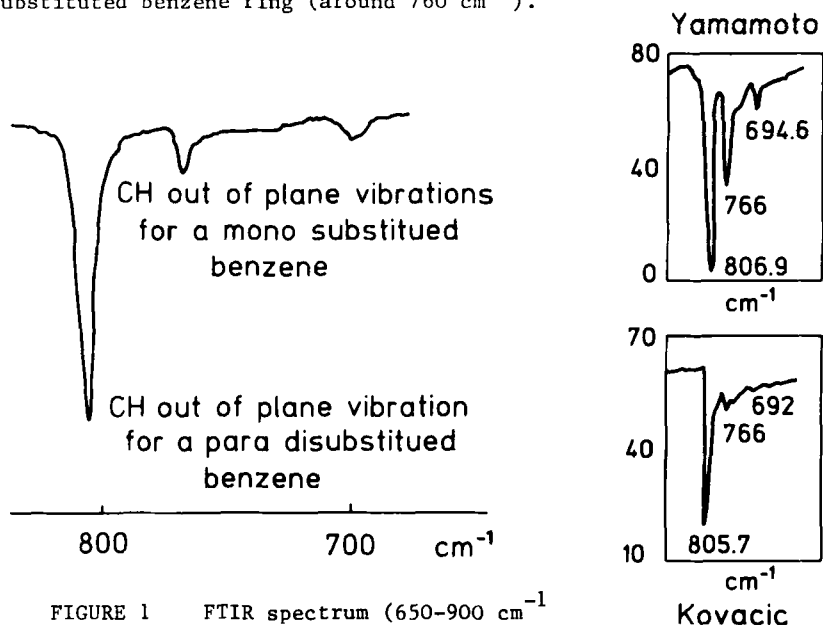


FIGURE 1 FTIR spectrum ($650\text{--}900\text{ cm}^{-1}$ region) of an electro poly(paraphenylene).

Inserts : for comparison IR spectra of Yamamoto and Kovacic PPP.

As compared to Yamamoto² and Kovacic¹ PPP spectra, one can see that the electropolymer spectrum is very close to that of the Kovacic PPP in terms of peaks maxima and intensities. This would indicate that this new PPP has fairly long chains.

Optical absorption

In figure 2, we have reproduced the optical absorption for the PPP synthesized by three different routes. It is to be noted that the maximum stands at $3.25\text{--}3.30\text{ eV}$ and the band edge at $2.85\text{--}2.90\text{ eV}$ for the electropolymer which is very similar to the values obtained for the Kovacic PPP.

Furthermore, this new PPP presents the same optical absorption curve as the Kovacic PPP.

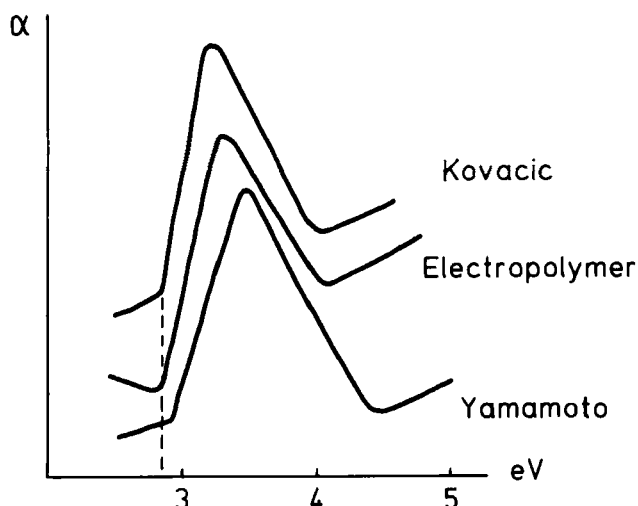


FIGURE 2 Optical absorption of poly(paraphenylenes) as a function of energy

These two features would mean that both polymers possess the same chain length distribution and that their average molecular weight are identical, which is in good agreement with the IR data.

Electron paramagnetic resonance

EPR experiments were run on the electropolymer powder using a standard X band spectrometer. The signal was symmetrical with $\Delta H_{pp} = 7.8$ to 8.7 Gauss and a g factor very close to that of the free electron as for other PPP. The spin concentration was determined thanks to a calibrated ruby. In the following table are summarized for comparison the data on the three PPP.

As can be seen, there is fundamentally no difference between the various PPP in terms of ΔH_{pp} , the linewidth is large, meaning that we are dealing with spins which are not moving⁸. The spin concentration remains low whatever the PPP sample. But it is very interesting to note that the electropolymer stands midway between the Kovacic and Yamamoto polymers, the spin concentration corresponds to 1 spin per roughly 10^6 (C_6H_4) units in this case which is very low.

	Electropolymer	Kovacic	Yamamoto
Spin concentration	2 to 7 10^{16} spins/g	10^{17} - 10^{18} spins/g	$< 10^{16}$ spins/g
ΔH_{PP}	7.8 - 8.7 G	6 G	7 - 7.5 G
d.c. conductivity at R.T.	$< 10^{-18} (\Omega\text{cm})^{-1}$	$< 10^{-16} (\Omega\text{cm})^{-1}$	$< 10^{-18} (\Omega\text{cm})^{-1}$
activation energy $\sigma = f(T)$	1.4 - 1.6 eV	0.9 eV	1.4 eV

DC Conductivity as a function of temperature

In order to get more information about the electropolymer we have recorded the d.c. conductivity as a function of temperature on several samples. The experiments were carried out under nitrogen in a cryostat specially designed to sweep a large temperature range + 200°C to liquid helium. The d.c. conductivity at room temperature is very low and could be estimated to $10^{-18} (\Omega\text{cm})^{-1}$. The $\sigma = f(T)$ fits more or less an Arrhenius plot or a $T^{-1/4}$ law, but the temperature range remains too narrow to discriminate the better fit inambiguously. Anyway, this polymer shows a high activation energy as compared to Kovacic PPP, this would mean, in connection with the very low d.c. conductivity at room temperature, that the electropolymer is very pure and that we are actually approaching the intrinsic properties of PPP. The above table collects some data on different poly(paraphenylene) in terms of d.c. conductivity.

DOPING

The first results obtained on AsF_5 -doped electropolymer indicate a d.c. conductivity at room temperature (four point probe method) ranging from 2 to 25 $(\Omega\text{cm})^{-1}$. The chemical doping was run under 100 mbar AsF_5 pressure at ambient temperature for 5 hours and lead to a doped material of general formula : $[\text{C}_6\text{H}_4(\text{AsF}_5)_{0.35-0.40}]$.

CONCLUSION

All the data we have developed and commented in this paper would indicate that the electropolymer cumulates the advantages of both Kovacic and Yamamoto poly(paraphenylenes). Long polymer chains bearing almost no defects with a high structural regularity makes the PPP synthesized by electrochemistry a very exciting electro-active polymer to work on. Further work is underway to gain more information about its properties.

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