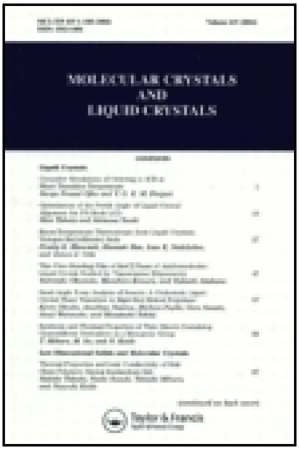

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ELECTRICAL TRANSPORT PROPERTIES OF MOLECULAR COMPOSITES DERIVED FROM THE OXIDATION OF POLY(N-VINYLPYRROLE)

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Consorzio Interuniversitario di Fisica della Materia: Progetto Materiali Polimerici

Abstract

Homo and copolymers of N-vinylpyrrole (NVP) were synthesized and the structure/properties relationships of the chemical oxidation products with $FeCl_3$ at different Fe^{3+}/NVP molar ratios characterized. From DC electrical, FT-IR and Raman spectroscopic characterizations, the picture of a composite at a molecular level emerges as that of a block copolymer of non-conducting and conducting segments, these last derived from the oxidation of PNVP. The possibility of giving an estimate of the growth of the oxidation level is seen from FT-IR data, whereas Raman spectroscopy seems to be specifically sensible to the modifications induced by the oxidation in the NIR-Vis absorption, probably coupled to the enhancement of the conduction process. The transport properties are analyzed according to the hopping model and the result of fitting procedures discussed.

INTRODUCTION

Conducting polymers are very promising materials for the perspective to apply the advantages of the processing techniques of plastics for manifacturing electronic devices electrical equipments.[1] A relevant part of the researches in the field is oriented to control the details of the molecular and supramolecular structures and to relate it to the electrical behaviour.[2]

The polymer precursor route has been used to improve the processability of electroconductive polymers.[3,4]

The oxidation of the insulating and soluble precursor polymer, poly(N-vinylpyrrole) [PNVP] (figure 1), prepared by radical polymerization of N-vinylpyrrole [NVP], produces an insoluble electro-conducting material with a polymeric ladder structure.[5]

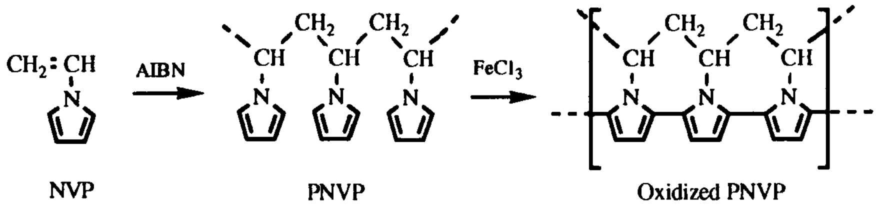

FIGURE 1 Synthesis and oxidation of poly(N-vinylpyrrole).

To obtain a better insight into the role of the macromolecular structure in determining electroconductivity, oxidized PNVP samples with different oxidation levels (Fe^{3+}/NVP feed molar ratio) were studied; moreover PNVP samples with different average molecular weight and NVP copolymers with styrene [STY], butylacrilate [BA] and o-methylstyrene [oMSTY] [6] and a 1:1 by weight PNVP/Polystyrene blend (PNVP/PolySTY) were oxidized.

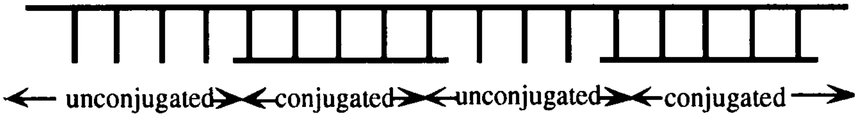

FIGURE 2 Structure of Electro-Conducting Molecular Composite [ECMC].

This synthetic strategy leads to the obtainment of a very special type of block copolymer where in the same macromolecule there are chemically linked conducting and insulating segments (figure 2), which are respectively conjugated PNVP segments and unconjugated chain segments made of unoxidized NVP units or non-oxidable comonomeric repeating units [STY, BA or oMSTY]. This system may be called an Electro-Conducting Molecular Composite [ECMC], differing from conventional composites and immiscible blends where interfacial interactions between different phases are mainly responsible for the dispersion of the components.

EXPERIMENTAL

NVP syntheses and homopolymerization were described elsewhere.[5,6] Copolymerization runs of NVP with STY, BA and oMSTY were carried out in toluene solution at 65 °C with α,α'-azobisisobutyrronitrile as radical initiator. After reaction the solvent was evaporated and the crude product purified by dissolution in $CHCl_3$ and precipitation with methanol.

The standard procedure for PNVP and NVP copolymers chemical oxidation is described as follows: to 100 mg of precursor polymer dissolved in 2 ml of CH_3CN, previously degased, such an amount of a degased aqueous acidic solution (0.6 N HCl) of $FeCl_3$ 0.6 N was added to obtain the desired Fe^{3+}/NVP molar ratio. The reaction mixture was stirred at 70 °C for 7 hrs; at the reaction end, the precipitated black powder was filtered under nitrogen and washed with water and acetone, then dried under vacuum.

The 1:1 (w:w) PNVP/Polystyrene blend was dissolved in CH_2Cl_2 and oxidized with the standard procedure above described.

Electrical conductivity measurements were performed on pellets in a controlled environment of argon with a four point-probe technique, using a Schlumberger Solartron 7081 Precision Voltameter and a Keithley 220 Current Source; temperature was measured by a Fluke 2190A digital Thermometer, using T thermocouples.

Raman spectra were recorded from pellets of PNVP diluted in solid KBr employing green and blue lines from an Ar+ ion CW laser (Coherent Inova 90) as exciting light and a scansion monochromator (Jobin Yvon Ramanor UV) equipped with an uncooled photomultiplier (EMI 9814) and digital photon counting electronics. IR measurements were performed with a Perkin-Elmer mod. 1600 serie FTIR spectrophotometer.

RESULTS AND DISCUSSION

The data reported in table 1 show that, as the Fe^{3+}/NVP molar ratio grows from 0.5 to 2.5, the conductivity increases up to the maximum value of 10^{-2} S/cm. The general higher conductivity values respect to those previously reported[6], are due to the improved samples preparation.

This trend can be understood in terms of the growing length and content of conjugated PNVP segments, as oxidation level increases.The oxidation of PNVP macromolecules with $DP_n > 15$ yielded a conducting polymer, while for $DP_n \leq 11$ insulating polymers were obtained ($\sigma < 10^{-9}$ S/cm) and this suggests the occurence of a threshold length such that a conjugated PNVP sequence contributes to the conduction process.[6] This hypotheses is also supported by the insulating character of oxidized copolymers of NVP with different non-oxidable comonomers such as styrene, butylacrilate and o-metilstyrene, where the insertion of statistically distributed or alternated non oxidable comonomeric units doesn't allow to gain the threshold. A further confirmation is provided by the good conductivity of the highly oxidized PNVP/polystyrene blend.

TABLE 1 Conductivity of oxidized PNVP and NVP copolymers samples.

Sample	Molar ratio Fe^{3+}/NVP	Yield (wt.%)	σ (S/cm)
POx0	0.50	55	$<10^{-9}$
POx1	0.75	107	$1.5\ 10^{-3}$
POx2	1.00	123	$1.8\ 10^{-3}$
POx3	1.50	119	$1.5\ 10^{-2}$
POx4	2.50	119	$2.5\ 10^{-2}$
NVP-co-STY 48:52	2.50	78	$<10^{-9}$
NVP-co-BA 60:40	2.50	12	$<10^{-9}$
NVP-co-oMSTY 83:17	2.50	22	$<10^{-9}$
PNVP/PolySTY	2.50	118	$1.9\ 10^{-3}$

IR and Raman spectra of PNVP samples, oxidized at a molar ratio Fe^{3+}/NVP ranging from 0.5 to 2.5 , were recorded and compared with those of the polymeric precursor.

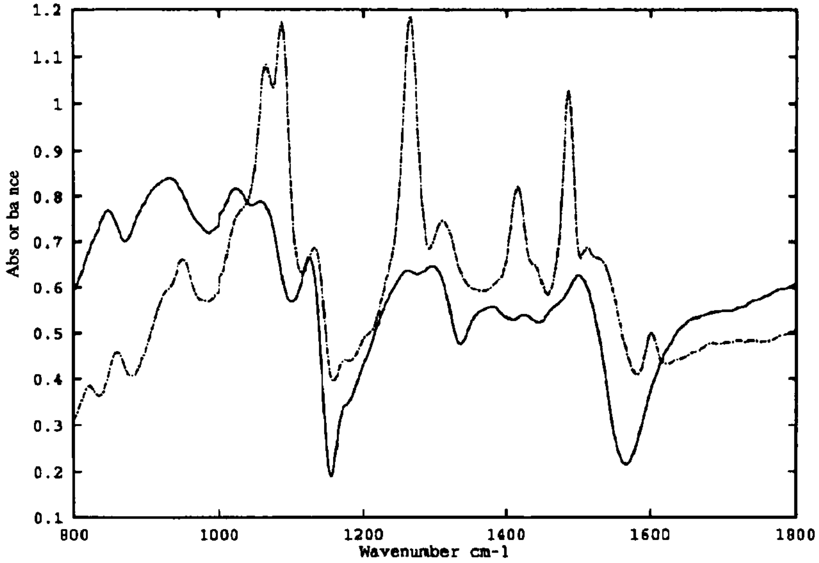

FIGURE 3 IR spectra of Oxidized PNVP with Fe^{3+}/NVP molar ratio 0.5 (dashed line) and 2.5 (solid line).

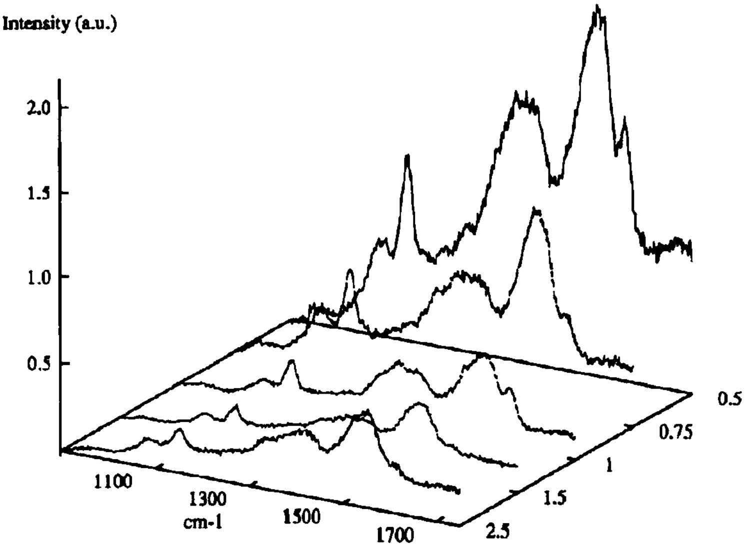

FIGURE 4 Raman spectra of oxidized PNVP versus Fe^{3+}/NVP molar ratio and versus frequency; excitation wavelength 514 nm.

Starting from an overall pattern similar to that of the precursor, the oxidized polymer IR spectra are widely modified as oxidation increases, both in band frequencies and intensities, as can be seen from figure 3, where the two extreme oxidation level IR spectra are reported. Therefore IR absorption may be viewed as a mixing of the conductive and non-conductive segments contributions from the molecular composite describing the oxidized polymer and hopefully may be used as an estimate of the oxidation level effectively obtained. On the other hand, the Raman spectra recorded for the same frequency region do not exhibit any significant shape variation as the oxidation level is increased, apart from a decreasing photoluminescence effect.[6] Moreover they differ so sharply from the polymeric precursor spectrum even at the lowest oxidation level that practically no Raman band of the last is found in the oxidized samples spectra. Thus the observed spectra may be due only to the conductive fraction of the molecular composite. This fact may be explained by a resonant enhancement mechanism arising from the NIR-Vis intragap absorption bands which are expected for a doped polymer.[7] While the exciting wavelength decreases from the green (514 nm) to the blue (458 nm), the Raman band intensities monotonically decrease for any fixed oxidation level in the investigated range, thus suggesting a "red peaked" resonant Raman enhancement. On the other hand, the whole Raman spectrum for any fixed excitation wavelength initially decreases, then reaches a minimum and newly grows up as the oxidant concentration is increased (figure 4), reminiscent of the non-monotonic behaviour of the ESR signal intensity.[6]

In short, while IR probes both the insulating and the conductive fractions of the molecular composite, Raman is resonant with the intragap electronic absorption of the conductive oxidized PNVP segments, probably determining the transport properties, and tends to probe them selectively.[8]

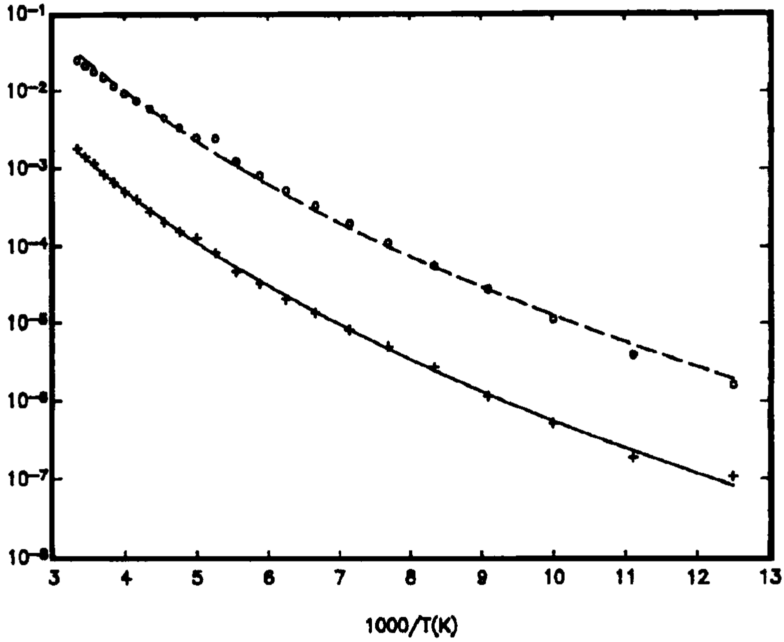

FIGURE 5 Experimental data and fitting curves of conductivity of oxidized PNVP samples with Fe^{3+}/NVP molar ratioes 1.0 (+) and 2.5 (o) vs temperature.

The conductivity as a function of temperature is shown in figure 5 for PNVP samples oxidized with Fe^{3+}/NVP molar ratio 1.0 and 2.5 in the temperature range from 80 to 300 K and reveals a behaviour substantially analogous to that of similar conducting polymers.[9] The hopping model was already adopted to describe the transport properties of highly oxidized PNVP [10]; following an analogous approach, the functional behaviour of Mott's variable range hopping in three dimensions [11]

$$\sigma(T) = \sigma_0 \exp\left\{-\left(\frac{T_0}{T}\right)^{1/4}\right\} \qquad (1)$$

was used to fit the experimental data, yielding a T_0 in substantial agreement with previous results[10] and not essentially dependent on the oxidation level of the sample; therefore the effect of different oxidation level seems to be mainly "stored" in the pre-exponential factor σ_0.

The structural picture of oxidized PNVP pointed out in this work leads to the understanding of the hopping process as the percolation of charge carriers through a path linking oxidized PNVP segments of length above the conduction threshold, either on the same or on a different macromolecular chain. Thus the occurrence of a further threshold, i.e. the percolation threshold, in terms of the fraction of oxidized PNVP segments that contribute to conduction vs. insulating PNVP segments may be inferred, as already shown by the insulating electrical character of low oxidation level samples.[6]

CONCLUSIONS

From the chemico-physical characterization of different EC polymer samples obtained by the oxidation of the precursor polymer PNVP to different extent, the peculiar picture of a molecular composite, consisting of conjugated doped blocks and non-oxidized NVP unit blocks seems to emerge. The electrical properties of the studied molecular composites are mainly determined by the length and the concentration of conjugated segments. The existence of a threshold conjugation length and threshold concentration of conjugated segments above the threshold length are inferred. The possibility of factorizing the effect of the oxidation level in the pre-exponential factor of variable range hopping.suggests a relevant influence of the oxidation level on the hopping distance and probability of charge carriers.[11]

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