Molecular control of electric conductivity and structural properties of polymers of pyrrole derivatives

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Abstract: The present paper describes some recent results concerning processable electroconducting materials prepared starting with properly substituted pyrrole derivatives. The first approach was based on the preparation of a precursor polymer by free radical polymerization of N-vinylpyrrole. This insulating, soluble and filmable polymer could be converted into an electroconducting product by intramolecular ladderization through oxidation of the pyrrole side chains. In the same frame the chemical homo and copolymerization of 3-decylpyrrole with pyrrole allowed to produce soluble or swellable polymers having conductivity variable with copolymer composition. The ladder formation and internal plastification by the long aliphatic side chain have been combined to give polymers derived from 3-decyl-N-vinylpyrrole and its copolymers with N-vinylpyrrole. Relationships between electroconductivity and controlled structure of the subject materials are discussed with reference to their blends with insulating plastomers.

INTRODUCTION

Pyrrole is one of the most used monomers for preparation of electroconducting polymeric materials. Indeed it offers several advantages such as the easy accessibility, the polymerizability, both by chemical or electrochemical oxidation, the good specific conductivity and chemical stability. On the other side its polymers are insoluble and intractable and therefore not useful for many specific applications.

The present paper reviews some recent results devoted to solve at least partially the above problems by preparing electroconducting polymers starting with properly substituted pyrrole derivatives.

The attractiveness of the selected polypyrrole system stems from several factors. The most important one is undoubtedly the chemical and thermal stability of these polymers relative to polyacetylene; the simple preparation and the possibility to prepare derivatives which have a range of appealing conductivity.

Further important features of the polypyrrole systems are the degrees of freedom available to modify the electrical and physical properties by resorting to derivatives, copolymers or particular doping agents in order to achieve any desired combination of polymer properties.

With the aim of improving the processability pyrrole derivatives suitable for preparing conductive polymers were used by adopting two different strategies. First the precursor polymer route in which a pyrrole monomer derivative is polymerized by a free radical reaction to a soluble and processable precursor, which can be oxidized to yield the desired conductive polymer. In this case a ladder polymer is obtained. The second route starts from 3-alkyl substituted pyrroles to be used in the preparation of homopolymers, copolymers, and blends.

PRECURSOR POLYMER ROUTE

By following the polymer precursor route a new conductive polymer has been obtained (1), which has been named oxidized poly(N-vinylpyrrole) (PNVP)

In the first step the PNVP is prepared by free radical polymerization of the N-vinylpyrrole monomer in the presence of azobisisobutyronitrile (AIBN) (Fig. 1). This polymer is soluble and processable but insulating.

$$CH_2 = CH \xrightarrow{\text{AIBN}} PNVP \xrightarrow{\text{FeCl}_3} \text{Oxidized PNVP}$$

NVP   PNVP   Oxidized PNVP
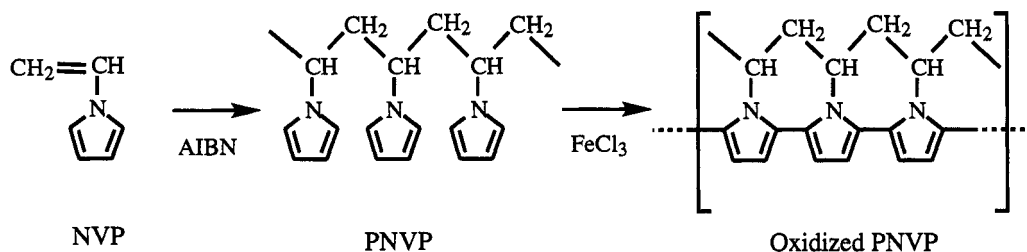
Fig. 1 Preparation procedure of the oxidized poly(N-vinylpyrrole).

In the second step the conjugated chain of pyrrole rings is formed by oxidation with iron trichloride solution. This procedure allows to control separately degree of polymerization (DP) and conjugated chain content.

In such a system the conduction mechanism can be sketched as for conductive polypyrrole and polythiophene. The conjugated chain has two phases (Fig. 2) for which the electronic ground states are not degenerate (due to the different length of bonds) so that the only stable defect is the polaronic one which introduces two localized levels in the band gap. Counterions and conjugated chain can exchange electrons giving charged polarons and bipolarons(2). Different polaronic states have different spin values: spin = 1/2 for charged polarons and spin = 0 for charged bipolarons.
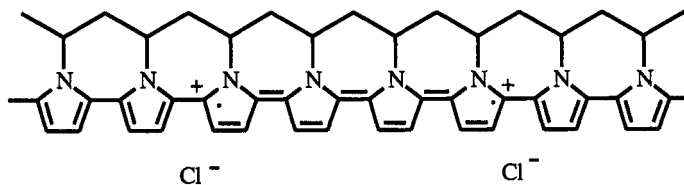
$$Cl^- \qquad\qquad Cl^-$$

Fig. 2 Schematic representation of a positively charged bipolaron.

In other words charge carriers are associated to structural defects of the chain: these carriers have a relatively low mobility in that they can move between different sites only by hopping. In this frame the charge transport mechanism can be related to electron jumping between localized states spatially distributed; in particular, for the system here considered, it has been proved that the jump probability takes into account for both-spatial and energy distances between localized states(3,4) (3-dimensional variable range hopping, 3D VRH).

By measuring the conductivity and the amplitude of the electron spin resonance (ESR) signal of samples of PNVP with DP = 54 (molecular weight = 5000) oxidized with different Fe^{3+}/NVP ratio, a sharp increase of the conductivity and of the ESR signal by increasing the Fe^{3+}/NVP ratio is observed. This behavior can

be ascribed to a growing concentration of charge carriers, i.e. charged structural defects, as doping level increases (Table 1). According to the strong ESR signal revealed at the relatively low doping level, these defects could be charged polarons, meanwhile at higher doping levels the conductivity saturation and the sharply decrease of the ESR signal indicate that the electronic charge carriers are mainly trapped in bipolaronic defects(5).

TABLE 1 Conductivity and ESR signal intensities of poly(N-vinylpyrrole) oxidized with different Fe^{3+}/NVP ratios

Sample	Molar ratio Fe^{3+}/NVP	Conductivity (S/cm)	Normalized Intensity of ESR signal
PNVP1	2.5	$4-9.2 \times 10^{-3}$	-
PNVP2	1.5	4.2×10^{-3}	2.3
PNVP3	1.0	4.2×10^{-4}	2.9
PNVP4	0.5	4.0×10^{-5}	8.9
PNVP5	0.25	1.5×10^{-9}	4.5

TABLE 2 Conductivity of poly(N-vinyl pyrrole) samples with different molecular weight oxidized with a Fe^{3+}/NVP ratio 2.5

Polymer	DP_n	Conductivity (S/cm)
PNVPA	4	insulator
PNVPB	8.6	insulator
PNVPC	11	insulator
PNVPD	16	3.2×10^{-3}
PNVPE	43	3.9×10^{-3}
PNVPF	54	4.2×10^{-3}

This important result can be simply obtained thanks to the procedure adopted for synthesizing the PNVP, i.e. precursor polymer route, which yields a conducting polymer whose oxidation level can be varied obtaining a partial oxidation product having substantially a block copolymer structure (Fig. 3).
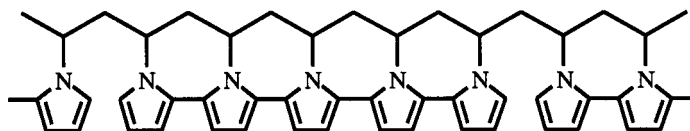

Fig. 3 Schematic structure of partially oxidized poly(N-vinylpyrrole).

In the case of polypyrrole, prepared by chemical oxidation of pyrrole, the polymer formed is highly conjugated for any oxidation ratio, so in this case the increase of this latter increases the polymer yield only. The conductivity remains substantially unchanged(6), apart of possible minor effects due to doping degree and molecular weight variation(5), and materials with different conductivity can be obtained only by a proper doping/dedoping procedure or oxidation by different systems.

The conductivity of PNVP samples having different degrees of polymerization (DP) but oxidized with the same Fe^{3+}/NVP ratio of 2.5 shows a sharp increase(7) at DP values around 16 (Table 2). This shows that electrical conductivity is possible only if a certain number of conjugated bonds is present allowing the conjugated chain to contain the polaronic distortion.

The existence of a critical chain length was predicted for polypyrrole by Bredas(2); his calculations provide an extension for the polaronic defect and a critical chain length quite comparable to that measured for PNVP.

The influence of the conjugation length along the macromolecular chain can be further demonstrated by the insulating characteristic of copolymers formed by conducting and insulating segments in the same macromolecule (Electro-Conducting Molecular Composites) (Fig. 4); for these systems the threshold conjugation length is probably never reached. On the contrary blends of the same polymers of comparable

composition show a semiconducting behavior thus confirming the presence of polaronic states even if the observed d.c. conductivity is probably allowed by tunnelling of the charge carriers trough insulating domains(8).
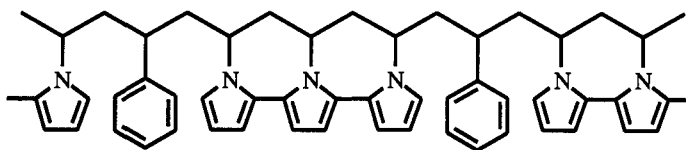

Fig. 4 Schematic structure of an Electro-Conducting Molecular Composite

POLYMERS OF 3-n.ALKYLPYRROLES

By following the second synthesis route, which starts from a 3-substituted alkyl pyrrole monomer(3DP), poly (3-decyl pyrrole) [P3DP] has been prepared by direct oxidation by $FeCl_3$ with the ratio $Fe^{3+}/3DP = 2.5$. The P3DP obtained is soluble in organic solvents due to the flexible alkyl side chain which on the other hand reduces the d.c. conductivity of this system; the d.c. conductivity measured at room temperature is about 0.5 S/cm and its temperature dependence is well fitted by 3D VRH equation(3,4). At a given temperature, the obtained d.c. conductivity of P3DP is much higher than for the oxidized PNVP; possibly in this latter materials the insulating vinyl chain reduces to a larger extent the interchain transfer of charge carriers than it does the alkyl side chain in the P3DP. Also a larger chain distortion and a reduced length of conjugated blocks is expected for oxidized PNVP as compared with P3DP.

In the case of poly(3-decylpyrrole) and 3-decylpyrrole/pyrrole copolymers, solubility is due to the long alkyl chains attached in the 3-position of pyrrole rings, as shown in the forthcoming structures:

P3DP   3DP/Py Copolymers
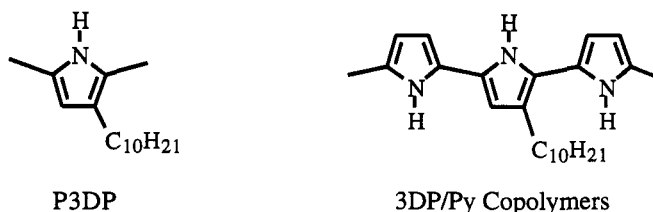
3-Decylpyrrole homopolymer, 3-decylpyrrole/pyrrole copolymers and pyrrole homopolymer were synthesized by chemical oxidation of corresponding monomers using various oxidants ($FeCl_3, CuCl_2, FeClO_4$), reaction solvents (methanol, acetonitrile, water) and temperature. The different polymerization conditions, and the copolymerization of alkyl substituted monomers with pyrrole, result in macromolecules having different structural regularity, average chain length, doping efficiency and distribution of paraffinic side chains. Electrical and solubility properties for 3-decylpyrrole/pyrrole copolymers of different composition are reported in table 3. It is clearly shown how it is possible to modulate copolymer conductivity between the two extreme values of 14.8 S/cm and 0.55 S/cm for pyrrole (PPy) and 3-decylpyrrole (P3DP) homopolymers, respectively; on the other hand the solubility of the material, particularly in $CHCl_3$ or CH_2Cl_2, is granted only if the molar content of 3DP is higher then 60%. In the solid state, 3-decylpyrrole/pyrrole conducting copolymers are black powder materials which differ in consistency depending on decyl side chain content; polypyrrole results in a fine rigid powder while P3DP is a soft powder with higher dimension particles.

TABLE 3 Electrical and solubility properties for 3-decylpyrrole/pyrrole copolymers

Polymer Sample	Py/3DP %mol.ratio	Conductivity (S/cm)	Solubility
PPy	100/0	14.8	insoluble
PPy3DP-60	39/61	4.8	high
PPy3DP-80	23/77	2.5	high
P3DP	0/100	0.55	total

An X-ray diffraction investigation of the microscopic structure and molecular organization of P3DP indicates a substantial pyrrole rings planarity with the alkyl group chain entangled out of the pyrrole ring plane, and the role of the dopant molecule in changing the gauche/trans populations within the n-decyl chain and affecting the formation of partially ordered aggregates(8).

N-VINYL-3-n.DECYLPYRROLE / N-VINYLPYRROLE COPOLYMERS

N-vinyl-3-decylpyrrole (NVDP), prepared starting from pyrrole, was then either homopolymerised or copolymerised with NVP by free radical initiators to yield a series of polymers (9) containing pyrrole side chains with variable amount of these last bearing the n-decyl group. These polymers schematically represented as below, had $\overline{Mn}$ in the range 3,200 - 7,200 corresponding to a number of monomeric residues ranging between 18 and 54.
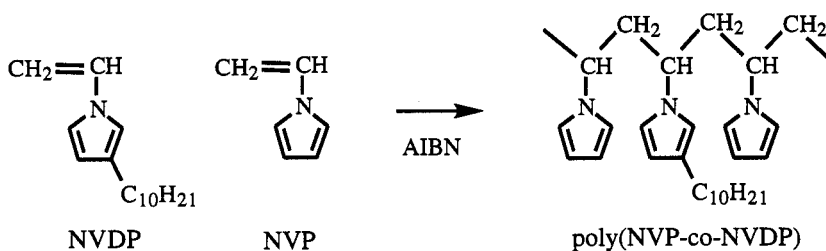
The treatment of these polymers with $FeCl_3$ gave in all cases a black material whose conductivity was increasing with augmenting NVP content, whereas solubility in organic solvents was decreasing correspondingly (Table 4). In particular, while oxidized poly(N-vinyl-3-decylpyrrole) was completely soluble in methanol, THF, $CHCl_3$ and dioxane at room temperature, oxidized poly(N-vinylpyrrole) was completely insoluble in organic solvents(1); indeed, when more then 60% of pyrrole rings are substituted with a decyl group, the corresponding oxidized N-vinylpyrrole/N-vinyl-3-decylpyrrole copolymer is soluble. Copolymers conductivity is depending not only on the composition, but also from the average polymerization degree; indeed copolymers with an higher polymerization degree have the major probability, after oxidation, to give polyconjugated chains with a length >15 pyrrole units, which was demonstrated as the threshold to achieve conductivity in PNVP systems(7). FT-IR spectra of oxidized PNVP, poly(NVP-co-NVDP)(1:4) and PNVDP are characterised by the presence of the tail of the bipolaronic intra gap bands, which tends to obscure proper IR phenomena in the range > 1850 cm^{-1}. In the case of NVDP homo- and copolymers, CH$_2$ stretching bands of decyl side chains clearly rise from the above mentioned "vibronic band".

TABLE 4. Oxidation of homo and copolymers of NVP and NVDP to ladder electro-conducting materials

Sample	NVDP in Copolymer (mol.%)	Solubility	Conductivity (S/cm)
PNVDP	100	+	5×10^{-7}
P(NVP-co-NVDP)(1:4)	81	+	3.3×10^{-5}
P(NVP-co-NVDP)(1:1)	61	+	5×10^{-6}
P(NVP-co-NVDP)(7:3)	46	+/-	1×10^{-4}
P(NVP-co-NVDP)(9:1)	9	-	1×10^{-2}
PNVP	0	-	2.5×10^{-2}

UV-Vis-NIR absorption spectra of the two homopolymers and of poly(PNVP-co-PNVDP)(1:4), after treatment with FeCl3, clearly show the presence either of gap bands (3.5 - 4.0 eV) and of polaronic-bipolaronic intra gap bands (1.4 - 2.6 eV). The previous data suggest the incomplete "ladderization" of pyrrole rings in homo- and copolymers and that the highest doping level has not been reached with the chemical oxidation process. The presence of two bands in the visible region is a peculiarity of these systems and has not been observed in soluble polypyrrole derivatives as poly(3-octylpyrrole)(10).

Indeed, the similarity of electronic spectra of different polymers are consistent with a similar degree of conjugation, the lower conductivity with NVDP units being probably due to distortion from planarity, that is confirmed by the shift to higher energies of the intra gap bands in optical spectra going from PNVP to PNVDP.

It is of interest to note that conductivity was linearly dependent on composition, thus suggesting a substantially homogeneous distribution of the two monomer units with formation of random copolymers chains. These data, while showing the possibility of modulating solubility and conductivity by copolymerisation of suitable comonomers, are in agreement with the formation of ladder structures by intramolecular conjugation of pyrrole side chains during the oxidation of N-vinylpyrrole derived polymers.

BLENDS

New materials prepared on compounding electroconductive polymer with thermoplastic or elastomeric polymers have been classified as composites, as the interactions between the two components are quite often limited to interfaces(11).

The approach in blends preparation on the other side is based on the attempt of obtaining at least a partial compatible blending thanks to the possibility of the establishment of intermolecular interactions between the functional groups of the two polymeric components. The obtainment of the above goal is favored firstly by dissolving the two components of the blend in a common solvent. In such a way potentially interacting functional groups are allowed to meet each other, and successively, by stripping quickly the solvent phase separation is minimized. This method of blend preparation may be applied only if the electroconducting polymer is processable. For the above considerations the electroconducting 3-decylpyrrole/pyrrole copolymer [PPy3DP-60] with a 3DP molar content of 61% was selected for blend preparations, EPR and EVA were chosen as non conducting polymer, because either Van der Waals interactions and/or hydrogen-bond-like interactions can be expected with the pyrrole polymers.

Both PPy3DP-60/EVA and PPy3DP-60/EPR blends, show increasing conductivity when the content in electroconducting polymer is increased, but there is a percolation threshold, corresponding to a weight

fraction of conducting polymers of 30% by wt. (17% by considering the conjugated structure, the polypyrrole backbone, only), under which the material is an insulator.

Since the trend of the curves is similar apart from EPR or EVA use, the conductivity does not appear to depend on the polarity and the dielectric constant of the non conducting partner. FT-IR examination shows that there is no strong interaction between carbonyl group of EVA and N-H group of pyrrole in PPy3DP-60, probably depending on the inability of the C=O group to give intermolecular interactions since it is very close to the backbone. Accordingly, the main interaction is probably of hydrophobic type between the hydrocarbon parts of the macromolecules (main chains of EPR or EVA and decyl groups of PPy3DP-60). Also the DSC analysis confirms the absence of strong interactions; for instance, the glass transition of EVA copolymer in blends does not change with composition, suggesting that insulating polymer domains are segregated from conducting polymer domains.

The morphology of the blends was studied by SEM analysis of film samples obtained by casting from CHCl3 solutions (12). SEM micrographs of blends characterized by 40,60,75% by wt. of electroconducting material show how the clusters of conducting polymers are surrounded and "wet" by the non conducting component. Links of 40-50 mm in length connect the clusters; the number and the thickness of links increase in samples characterized by an higher concentration of conducting polymer. In these bridges the conducting polymer is spread, as confirmed by the Chlorine counterions mapping. Moreover, the Chlorine-microanalysis of the blend characterized by 25 % by wt. of electroconducting material shows that in this case there is no connection path, and thus the mixture is not conductive with PPy3DP-60 totally dispersed in the insulator matrix.

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