Synthesis, structural characterization and electrical properties of highly conjugated soluble poly(furan)s*

Federica Benvenuti, Anna Maria Raspolli Galletti, Carlo Carlini† and Glauco Sbrana
Dipartimento di Chimica e Chimica Industriale, University of Pisa, Via Risorgimento 35, 56126 Pisa, Italy

and Andrea Nannini and Paolo Bruschi
Dipartimento di Ingegneria dell'Informazione, Elettronica, Informatica, Telecomunicazioni, Via Diotisalvi 2, 56126 Pisa, Italy

The polymerization of furan by different oxidants has been studied. Particular attention has been devoted to the nature of the reaction medium in combination with $FeCl_3$ as oxidizing agent. The use of a polar aprotic solvent with high donicity, such as propionitrile, allows one to obtain soluble oligo(furan)s with an ordered aromatic structure and hence high conjugation degree. These products, when blended with polar polymers such as poly(ethylene-co-vinyl acetate), give rise to films with good mechanical properties which, after I_2-doping, display electrical conductivity of several orders of magnitude higher than that reported up to date for I_2-doped powdery and intractable poly(furan)s. © 1997 Elsevier Science Ltd.

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INTRODUCTION

In the last decade, electroconducting polymers derived from heterocyclic monomers, such as thiophene and pyrrole, received a great deal of interest[1–4] because their high conductivity in the doped state was accompanied by a much higher stability in air with respect to poly(acetylene). More recently, soluble and processable highly conducting poly(3-substituted thiophene)s[5–8] and poly(3-substituted-pyrrole)s[9–12] were obtained by attaching long flexible side chains on to the conjugated backbone, thus overcoming the main drawback of the previous polymeric systems, usually consisting of intractable, infusible and insoluble materials and hence not useful for real applications.

On the other hand, much less attention has been devoted up to date to the synthesis and characterization, in terms of structural and electroconducting properties, of poly(furan)s, probably because of their supposed less well-defined structures and poor stability. Indeed, earlier studies on the polymerizability of furan by cationic initiation[13–16] have permitted one to establish that the resulting polymer had lost the most part of aromaticity, the backbone being mainly constituted by 2,3-dihydro-2,3-furylene (I) and 3-(2-furyl)-tetrahydro-2,5-furylene (II) units, responsible for low conductivity.


(I)   (II)
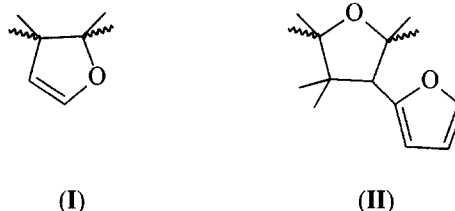
Another synthetic approach, scarcely explored, was the oxidative coupling of furan and 2-methyl-furan, promoted by palladium salts in acidic solvents, to give dimeric products. In particular, the addition of a redox system in order to obtain a catalytic process was also investigated[17]. However, the acidity of the medium caused extensive oxidative degradation of the products, thus strongly reducing selectivity and yield of the reaction. More promising appeared to be the oligomerization of furan in the presence of catalytic amounts of $RuCl_3.xH_2O$, in anhydrous ethanol, to give dimers and trimers[18]. Also in this case, however, the process would need to be improved in order to obtain products with higher molecular weight and electrical conductivity.

The polymerization of furan by electrochemical oxidation was also investigated[19–23]. Nevertheless, it was observed that, due to the high oxidation potential of furan, a significant cleavage of the furan ring occurred during the electropolymerization, thus strongly shortening the expected polyconjugated structure (III).

(III)
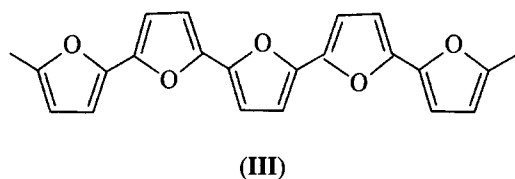
Finally, the chemical oxidative polymerization of furan was reported to afford a black intractable powder with quite poor electroconductive properties[24,25]. Indeed, although only anhydrous aprotic solvents must be used in combination with strong Lewis acids as oxidants, traces of acid in the medium cannot be avoided, thus promoting both cleavage and cationic polymerization of the furan rings to give, in addition to sequences III, 1,4-diketone units[26] (IV) and the above-mentioned I–II units, respectively.

(IV)
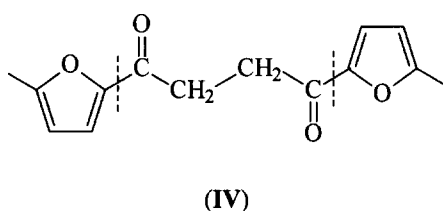
In this context, taking also into account that furan is expected to be easily available in the recent future by oxidative degradation processes from sugars, polysaccharides and renewable materials of agricultural origin[27,28], the aim of this research work is to reinvestigate the oxidative polymerization of furan by means of Lewis acids, with particular reference to the use of polar aprotic solvents, in order to obtain poly(furan)s with controlled structure, in terms of a very high content of aromatic units, and lower molecular weights, these intrinsic characteristics being essential for the production of soluble and processable materials having significant electroconducting properties.

EXPERIMENTAL

Reagents and solvents

Furan (Fluka) was dried on 4 Å molecular sieves, then refluxed for 8 h over sodium and finally distilled under anhydrous argon.

$FeCl_3$ and I_2 (Carlo Erba) were dried by sublimation and stored under anhydrous argon. Chloroform and methylene chloride (Merck) were washed with water, dried over anhydrous $CaCl_2$, refluxed over CaH_2 for 4 h and finally distilled under dry argon.

Acetonitrile and propionitrile (Carlo Erba) were dried on 4 Å molecular sieves, then refluxed over CaH_2 for 4 h and finally distilled under dry argon.

Absolute ethanol: the commercial product (Carlo Erba) was dried according to the Lund and Bjerrum procedure[29]. The product was finally distilled under dry argon.

Hexane (Carlo Erba) was dried on 4 Å molecular sieves, then refluxed over Na/K alloy and finally distilled under dry argon.

$NOBF_4$ and $NOSbF_6$ (Strem) were used as received and handled under dry argon.

Poly(ethylene-*co*-vinyl acetate) (57 mol% of ethylene units), commercial product Levapren 700 from Bayer, and sodium citrate (Carlo Erba), were used as received.

2,2′,5′,2″-Terfuran (TFU) was prepared as previously described[30].

Infrared (i.r.) spectrum (cm^{-1}): 3127, ν_{C-H}; 1615, $\nu_{C=C}$; 1160, $\delta s_{C=C}$; 1087, $\delta a s_{C=C}$; 1008, ν_{C-O-C}; 787, δ_{C-H}. Proton nuclear magnetic resonance (^{1}H n.m.r.) (CDCl$_3$): $\delta = 7.48$ ppm (*d*, 2H, H-5 and H-5″ of terminal furan rings); 6.62 ppm (*d*, 2H, H-3′ and H-4′ of central furan ring); 6.58 ppm (*d*, 2H, H-3 and H-3″ of terminal furan rings) and 6.42 ppm (*m*, 2H, H-4 and H-4″ of terminal furan rings).

Carbon-13 n.m.r. (CDCl$_3$): $\delta = 147.4$ ppm (quaternary carbons in the central furan ring); 145.8 ppm (quaternary carbon in terminal furan rings); 142.3 ppm (C-5 and C-5″ in terminal furan rings); 112.8 ppm (C-4 and C-4″ in terminal furan rings) and 107.0 ppm (C-3 and C-3″ in terminal furan rings) and 104.6 ppm (C-3′ and C-4′ in central furan ring).

Polymerization of furan by chemical oxidative processes

A general procedure is described as follows. The Lewis acid, dissolved in the appropriate solvent, was introduced under dry argon at room temperature, into a two-necked 100 ml flask, equipped with reflux condenser, dropping funnel and magnetic stirrer, then furan was added dropwise (molar ratio of Lewis acid/furan ≈ 1.4). The reaction mixture immediately became black and, when CHCl$_3$ or CH$_3$NO$_2$ (alone or in combination with CH$_2$Cl$_2$) were used as solvent, both black precipitate and film deposited on the flask walls were obtained. In the presence of CH$_3$CN as solvent only the formation of a black polymeric film was observed, in addition to the black solution. On the other hand, when C$_2$H$_5$CN was used as reaction medium only a black solution of the polymerization product was obtained. In all cases the reaction was interrupted after 3–4 h.

The polymerization product was isolated by filtration, under dry argon, when CHCl$_3$ or CH$_3$NO$_2$ were used as reaction solvents. In the case of CH$_3$CN the reaction mixture was evaporated to dryness and the solid product washed several times with absolute ethanol. Finally, in the presence of C$_2$H$_5$CN as polymerization medium, hexane was added to the reaction mixture and this was extracted with a saturated aqueous solution of sodium citrate. The organic layer was dried on 4 Å molecular sieves and finally evaporated to dryness. A brown solid was obtained. For more details see *Table 1*.

All the polymeric products were characterized by Fourier transform infrared (*FT*i.r.) analysis, and the soluble ones were also submitted to ^{1}H and ^{13}C n.m.r. analyses.

Procedures for the removal of inorganic salts from the pristine polymers

The polymers obtained with FeCl$_3$ in CHCl$_3$ and CH$_3$CN (PFu.Cl and Pfu.AN, respectively) were submitted, in a Kumagawa apparatus, to continuous extraction with boiling absolute ethanol in order to eliminate ferric and ferrous salts and obtain the polymers in the corresponding neutral form (PFu.Cl.E and PFu.AN.E). After this treatment, ochre-coloured powders were obtained from the corresponding pristine black and hygroscopic powdery materials. In the case of the polymeric sample obtained by FeCl$_3$ in the presence of propionitrile as reaction medium, the isolation of the polymer from its solution after extraction of the ferric

Table 1 Synthesis of poly(furan)s by polymerization in the presence of different oxidants and solvents[a]

Run	Oxidant Type	Amount (mmol)	Solvent Type	Volume (ml)	Furan (mmol)	Polymeric product Type	Weight (g)
1	$FeCl_3$	35.0	$CHCl_3$	50	25.0	$PFu.Cl^b$	3.3
2	$FeCl_3$	22.0	CH_3NO_2	18	15.0	$PFu.NM^b$	1.5
3	$FeCl_3$	30.0	CH_3CN	45	20.6	$PFu.AN^c$	1.8
4	$FeCl_3$	42.0	C_2H_5CN	60	30.0	$PFu.PN^d$	0.9
5	I_2	9.9	—	—	40.0	$PFu.I^c$	1.7
6	$NOBF_4$	7.2	$CH_2Cl_2/CH_3NO_2{}^e$	100	5.5	$PFu.NB^b$	0.4
7	$NOSbF_6$	4.8	$CH_2Cl_2/CH_3NO_2{}^e$	120	3.6	$PFu.NS^b$	0.4

[a] Duration: 4 h for runs 1–5 and 3 h for runs 6 and 7
[b] After washing with the reaction solvent
[c] After washing with absolute ethanol
[d] After treatment with 10 ml of hexane and extraction with 3 portions (10 ml each) of a sodium citrate saturated aq. solution
[e] 1/1 (v/v) Mixture

Table 2 Undoped poly(furan)s obtained from the corresponding pristine polymers after extraction procedures

Pristine polymer	Cl^a	D^b	Extraction with	Undoped polymer	Yield[c] (%)	Cl^a	D^b
PFu.Cl	95	3.5	Abs. ethanol[d]	PFu.Cl.E	71	1	∼ 100
PFu.AN	88	3.4	Abs. ethanol[d]	PFu.AN.E	65	0.7	∼ 100
PFu.PN	n.d.[e]	n.d.	Sodium citrate aq. soln[f]	PFu.PN.E	46	2.2	∼ 99
PFu.I	—	—	Abs. ethanol[d]	PFu.I.E	67	—	—

[a] Expressed as $(meq\,g^{-1}) \times 10^{-1}$
[b] Molar ratio between neutral and doped units
[c] Determined with respect to the monomer
[d] 24 h at the boiling temperature
[e] Not determined
[f] At room temperature

and ferrous salts with a saturated aqueous solution of sodium citrate allowed one to obtain directly the polymer in the neutral form. Therefore, PFu.PN, after its recovery by this procedure, has to be considered as PFu.PN.E. For details see *Table 2*.

Doping procedures for the neutral polymers by iodine

The doping was performed either by using an I_2 solution in heptane or exposing a film of the polymer to I_2 vapour. In the first case, weighed amounts of PFu.Cl.E, PFu.AN.E and PFu.I.E, as powders, were introduced, under dry argon, into a Schlenk vessel containing 25 ml of an I_2 (0.06 M) solution in heptane. The polymeric suspension was maintained at room temperature under magnetic stirring for 2 h. The doped polymer was filtered, washed with heptane and finally dried for 15 min *in vacuo*. The I_2 uptake was gravimetrically determined. In the second case, films of PFu.PN.E or PFu.PN.E/poly(ethylene-*co*-vinyl acetate) blends, deposited on a glass support by the solution spinning technique, were introduced under dry argon into a two-necked flask. After evacuation at 0.1 mmHg, the flask was connected for 4 h to a Schlenk vessel containing I_2 at 50°C $(P_{I_2} = 4\,mmHg)$. After removal of excess of I_2 from the polymer film by an argon stream, the I_2 uptake was gravimentrically determined.

Chloride analysis in poly(furan)s

The pristine poly(furan)s prepared by $FeCl_3$ in different solvents (PFu.Cl and PFu.AN) as well as the

neutral polymers (PFu.Cl.E, PFu.AN.E and PFu.PN.E) were characterized by chlorine content. The general procedure involved alkaline fusion with sodium peroxide of a weighed polymer sample, the addition of distilled water until a certain volume of aqueous solution was obtained and titration of the chloride content by $AgNO_3$, according to the Mohr method[31].

Physicochemical measurements

The ^1H and ^{13}C n.m.r. spectra were recorded at 200 and 50.3 MHz, respectively, by a Varian Gemini 200 spectrometer in $CDCl_3$ or $DMSO$-d_6 solutions, using tetramethylsilane as internal standard.

The *FT* i.r. spectra were recorded on a Perkin-Elmer Model 1750 spectrophotometer. The samples were prepared as KBr pellets or as cast films on KBr discs.

Average number molecular weights of the soluble polymers were determined at 30°C in 1,2-dichloroethane by a Wescam Model 233 vapour pressure osmometer. The calibration curve was obtained with solutions at different concentration of saccharose octaacetate.

Thermogravimetric analysis (t.g.a.) was carried out, under an inert atmosphere, by a Mettler TA4000 calorimeter at a heating rate of $10°C\,min^{-1}$.

Thin polymer films were obtained with a spinning procedure on 10% (w/w) polymer solutions by means a Zelpro PRS-5V spinner apparatus. The film thickness and its homogeneity were measured and checked by a Tencor Instruments Alpha Step 200 profilometer.

Electroconduction measurements were carried out on 1 mm thick polymer pellets having a 1 cm^2 section. The pellets were obtained by weighing identical amounts of polymer and pressing at 200 bar. Otherwise, polymer films of known thickness, obtained by solution spinning, were used. For samples having resistivity lower than 300 MΩ the current was monitored by a Keithley Model 199 electrometer. The samples having resistivity higher than 300 MΩ were analysed by monitoring the current with a HP-4145B semiconductor parameters analyser.

RESULTS AND DISCUSSION

*Oxidative polymerization of furan: influence of the nature of oxidant and reaction medium*

The polymerization of furan has been preliminarly performed by FeCl$_3$ at room temperature using CHCl$_3$ as reaction solvent (run 1, *Table 1*).

In these conditions a black polymer, both as a powdery suspended material and a film deposited on the reaction vessel, was obtained. The polymer (PFu.Cl), completely insoluble in the most common organic solvents, also remained black after repeated washings with anhydrous chloroform, thus suggesting that it was obtained in the oxidized form. Indeed, FeCl$_3$ is able not only to promote, by a redox process, the oxidative coupling of furan rings, but also to extract electrons from the polymer backbone to afford a polymer complex in which inorganic species, such as Cl$^-$ and FeCl$_4^-$ are present as counter-ions. Moreover, the excess of FeCl$_3$ and its reduction products probably remain embedded in the polymer during its precipitation. This hypothesis is confirmed by t.g.a. of PFu.Cl, which shows (*Figure 1*) a progressive weight loss (about 40%) due to evaporation of non-chemically bonded FeCl$_3$ below 500°C, the temperature at which the degradation of the polymer starts to occur.

A further confirmation to this picture derives from electrical characterization of PFu.Cl. Indeed, the current intensity of the material *versus* the applied voltage does not show a linear trend as in the case of an ohmic behaviour, thus suggesting the presence of ionic species responsible for electrolytic phenomena. Moreover, when a zero voltage was applied to the material an appreciable current was monitored, according to the presence of a redox process. Finally, the electrical conductivity of PFu.Cl was found to be in the 10^{-6}–10^{-5} S cm^{-1} range, appreciably higher than that reported[21,23,24] for the doped polymer prepared by FeCl$_3$ in chloroform

solution (10^{-7}–10^{-9} S cm^{-1}), and therefore in agreement with the presence of additional ionic conductivity. However, the observed electrical conductivity is in absolute value quite low for a doped highly conjugated polymer, thus suggesting the presence of non-aromatic units, which do not allow an extensive conjugation along the backbone.

Accordingly, the *FT* i.r. spectrum of PFu.Cl shows (*Figure 2*) bands at 3124 and 2932–2872 cm^{-1}, assignable to the stretching vibrations of C–H bonds, indicative, respectively, of aromatic sequences **III** as well as of dihydro- (**I**) and tetrahydro-furylene (**II** and **V**) units.
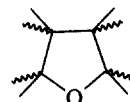

V

Moreover, the presence of a band of significant intensity at 1708 cm^{-1}, related to the C=O stretching of carbonyl groups, suggests that the cleavage of furan rings also occurs to afford **IV** units. The existence of aromatic sequences **III** is also confirmed by the presence of bands at 1160 and 1087 cm^{-1}, typical of symmetric and asymmetric C=C bending in furan rings in that order, as well as of bands at 1012 and 790–733 cm^{-1}, characteristic of C–O–C plane deformation and C–H out-of-plane bending of the furan ring, respectively. Finally, the band at 884 cm^{-1}, connected with the C–H bending in olefinic systems, is also present.

In conclusion, in PFu.Cl, sequences of aromatic units **III** are randomly distributed along the backbone in a more complex structure consisting also of dihydro- and tetrahydro-furylene units **I**, **II** and **V** as well as of open chain units **IV**.

Therefore, the i.r. analysis clearly indicates that the polymeric product is the result of two distinct processes, the former causing oxidative coupling to afford repeating aromatic units and the latter involving cationic species, responsible for the presence of non-aromatic units. Indeed, in the oxidative coupling of furan, 2 H$^+$ equivalents are released in the reaction medium for each event, thus making possible both the cationic polymerization and the cleavage of furan rings.

In order to remove from the pristine polymer the ferric and ferrous chlorides, responsible for the ionic conductivity, PFu.Cl was submitted to extraction with boiling absolute ethanol (see Experimental). The polymer (PFu.Cl.E), after extraction, changed from black to ochre coloured, thus suggesting a neutral form. In order to confirm the netural state of the polymer after this treatment, chloride analysis was performed on the polymer samples before and after the extraction procedure. On the basis of the above data and assuming that the doped units in the polymer are represented by structure **VI**, it was possible to determine the molar ratio *D* between neutral and doped units in the polymer samples.
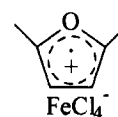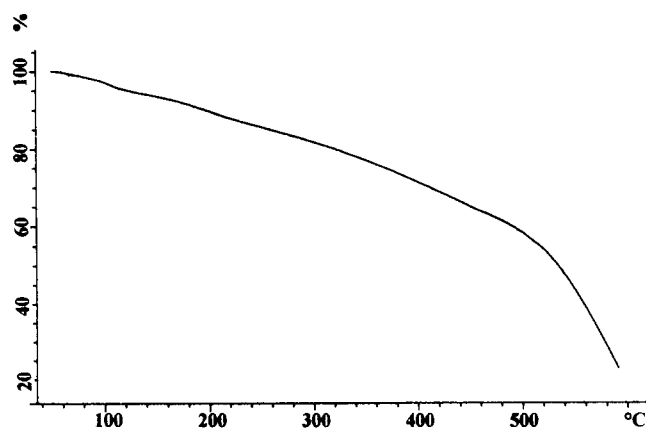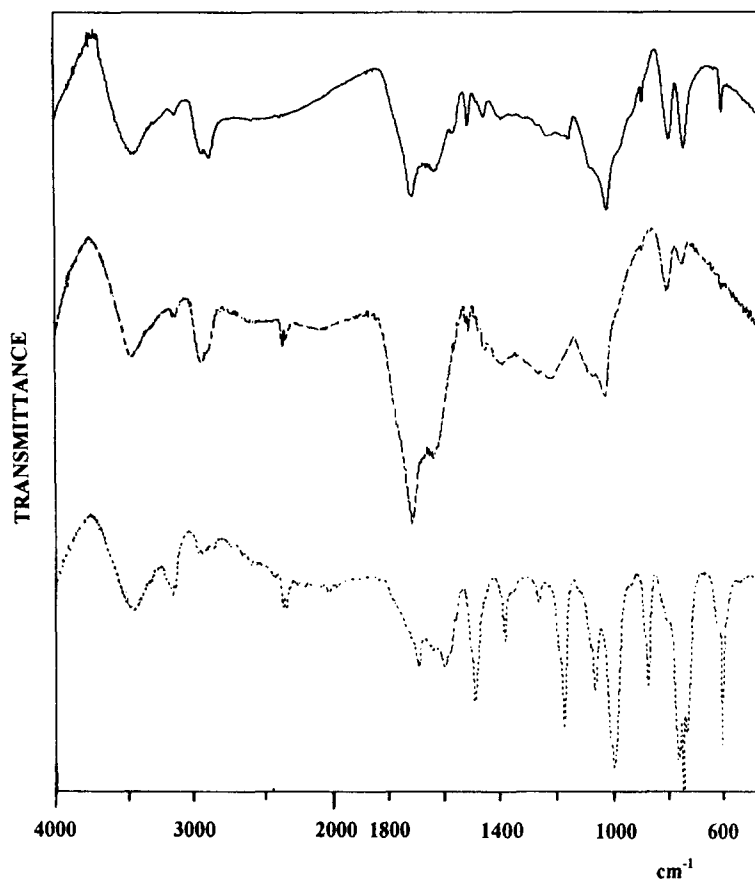

Figure 1   Thermogravimetric curve for PFu.Cl

FeCl$_4^-$

VI

Figure 2 *FT* i.r. spectra of: (———) PFu.Cl (KBr pellet); (- - - -) PFu.Cl.E (KBr pellet); (·····) PFu.PN.E (film on KBr disc)

As reported in *Table 2*, PFu.Cl, having an initial *D* value of 3.5, after the extraction procedure gives rise to PFu.Cl.E, which appears substantially neutral, *D* being about 100.

The i.r. spectrum of PFu.Cl.E (*Figure 2*) displays all the most relevant bands observed for the pristine polymer, thus confirming that its structure is quite complex and consists of random sequences of the aromatic and non-aromatic units previously mentioned.

Analogous results were obtained (*Table 1*) by using as oxidants nitrosyl tetrafluoroborate and hexafluoroantimonate in mixed CH_2Cl_2/CH_3NO_2 solvents. Indeed, in both cases black insoluble polymers (PFu.NB and PFu.NS) were obtained having i.r. spectra quite similar to that reported for PFu.Cl.

Also, I_2 afforded in bulk (*Table 1*) a black insoluble polymer (PFu.I), whose i.r. characteristics are very similar to those of PFu.Cl.

The above data clearly indicate that when strong oxidants are used in solvents with a poor donicity[32], such as $CHCl_3$ and CH_2Cl_2/CH_3NO_2, only insoluble poly(furan)s with uncontrolled structure are obtained. On the other hand, if initiators with a lower oxidative capability are employed, such as $CuCl_2$, due to the high oxidation potential of furan[20-22], no polymer is obtained.

In order to drive the oxidative polymerization of furan in the direction of a better control of the polymer structure, in terms of both molecular weight and sequences of aromatic units, the influence of the reaction medium has been investigated by using $FeCl_3$ as oxidant.

It is well established that apolar solvents are not efficient in promoting the polymerization, probably

because of the insolubility of $FeCl_3$ in the reaction medium. Moreover, polar protic solvents cannot be used as they cause acid generation by $FeCl_3$ hydrolysis, thus favouring both cationic polymerization and cleavage of furan to give undesirable non-aromatic units. Therefore, taking into account that polar solvents with poor donicity do not afford the desired polymeric products in the presence of $FeCl_3$, as described before, we have examined the effect on furan polymerization of polar aprotic solvents with high nucleophilic character. Indeed, the use of these last solvents is expected to increase, by coordination, the solvation of the oxidant, thus reducing its Lewis acidity and hence its cationic polymerization capability. In these conditions, aromatic structures **III** should prevail and the degree of conjugation of polymer backbone should be also improved.

In this context, nitromethane, acetonitrile and propionitrile, having increasing donor properties in that order[32], have been checked (*Table 1*). When CH_3NO_2 (run 2) was used in combination with $FeCl_3$, a black polymeric material (PFu.NM), both as powder and deposited film, was obtained whose i.r. spectrum was substantially similar to that found for the polymer prepared in chloroform (PFu.Cl). Analogous results were observed for PFu.AN, obtained in CH_3CN (run 3). In contrast, when C_2H_5CN was used as reaction medium (run 4) only a black soluble polymer (PFu.PN) was obtained. PFu.PN was converted into the neutral form by extracting the reaction mixture at room temperature with an aqueous solution of sodium citrate to afford PFu.PN.E as an ochre-coloured solid material, but still soluble in the most common organic solvents. Elemental analysis, based on chlorine content (*Table 2*), has

allowed us to confirm that PFu.PN.E is substantially undoped, the ratio between neutral and doped units being about 99.

The i.r. spectrum of PFu.PN.E shows (*Figure 2*), in the 2930–2870 cm^{-1} region related to C–H stretching of aliphatic compounds, a much weaker band as compared with the previously obtained poly(furan)s, thus suggesting a very high content of aromatic units in the polymer. Moreover, the band at 1691 cm^{-1} related to C=O stretching of carbonyl groups, despite its high optical density, shows a quite low intensity, thus proving that 1,4-diketone unis **IV** are almost absent in this polymer.

A further characterization confirming the above picture can be done by ^{1}H n.m.r. analysis based on the protons' assignment of TFU, properly synthesized as model compound (see Experimental). Indeed, PFu.PN.E displays a signal, centred at about 7.5 ppm, related to the protons in the α-position to the heteroatom in the terminal furan rings. Moreover, in the 6.5–6.3 and in 6.3–6.0 ppm regions two broad signals are present, assignable to the protons in the β-position to the oxygen of furan rings in internal and terminal units, respectively.

Finally, the absence of signals of significant intensity below 5 ppm, where aliphatic protons are located, confirms that **I**, **II**, **IV** and **V** units are not detectable, thus suggesting that aromatic structures **III** largely prevail and the polymeric material is highly conjugated.

Also, the ^{13}C n.m.r. spectrum (*Figure 3*) agrees with the proposed structure. Indeed, on the basis of the analogous spectrum of TFU (see Experimental), the signals in the 105–110 ppm region may be assigned to the carbon atoms in the β-position to the heteroatom of furan rings in the internal units, whereas the signal at 110.2 ppm is related to the same carbons in the terminal furan rings, where the shielding effect is lower. Moreover, the signals around 141–142 ppm may be assigned

to the carbon atoms in the α-position to the oxygen in the terminal furan rings. Finally, the quarternary carbon atoms in the α-position to the heteroatom, both in the terminal groups and in the polyconjugated chain, are located in the 154–155 ppm region. It is worthy of note that no appreciable signals are present either in the 190 or the 20–60 ppm regions, connected with carbon atoms of carbonyl groups, as in 1,4-diketone units, and of dihydro- and tetrahydro-furylene units, respectively. Therefore, these findings further confirm that PFu.PN.E consists essentially of a highly conjugated structure **III**.

The comparison between the integrated areas of protons at 7.55 and at 6.0–6.5 ppm may also allow one to determine the number average polymerization degree ($\bar{X}_n$) of the system, which is found to be about 8, corresponding to a number average molecular weight ($\bar{M}_n$) of about 530 daltons. This value is substantially in agreement with that found directly by vapour pressure osmometry ($\bar{M}_n = 590 \pm 30$ daltons).

Therefore, we have to conclude that PFu.PN.E has be considered as an oligomeric product, as represented below:

n = 6-7
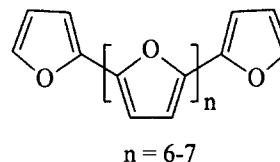
Electrical conductivity properties of poly(furan)s in the neutral and doped state

As previously mentioned, the obtained poly(furan)s have been submitted to extraction in order to remove the excess of FeCl$_3$, which is responsible for ionic conductivity of the polymer sample. After the extraction the polymers are substantially obtained in the neutral state. PFu.Cl.E and PFu.AN.E, which consist of insoluble powdery materials, have been submitted to electrical conductivity measurements as pressed pellets. As reported in *Table 3*, their conductivity is very low ($\sigma \approx 10^{-13}$ S cm^{-1}), thus confirming the absence of charge carriers in the above materials.

In contrast, PFu.PN.E, a soluble material, has been deposited as a film over a glass substrate by a solution spinning technique. Unfortunately, the obtained film is very brittle and inhomogeneous in terms of thickness, as the sample has the tendency, during evaporation of the solvent, to give microcrystalline aggregates with a very poor plasticity, due to the too low molecular weight of the system. In these conditions it was not possible to obtain reliable data for conductivity, which, however, were below the limits of detection, thus confirming that PFu.PN.E is substantially a neutral material.

When for PFu.CL.E and PFu.AN.E the current intensity was measured as a function of the applied voltage (0–30 V) for different temperatures (70–180°C) a linear trend was observed, thus clearly indicating that the samples show an ohmic behaviour, hence excuding the presence of ionic conductivity. In particular, for both the neutral polymer samples, it was observed that at zero applied voltage no current was detected, thus excluding the presence of any redox process, as in a cell. As an example in *Figure 4* the electrical behaviour of PFu.Cl.E is reported.
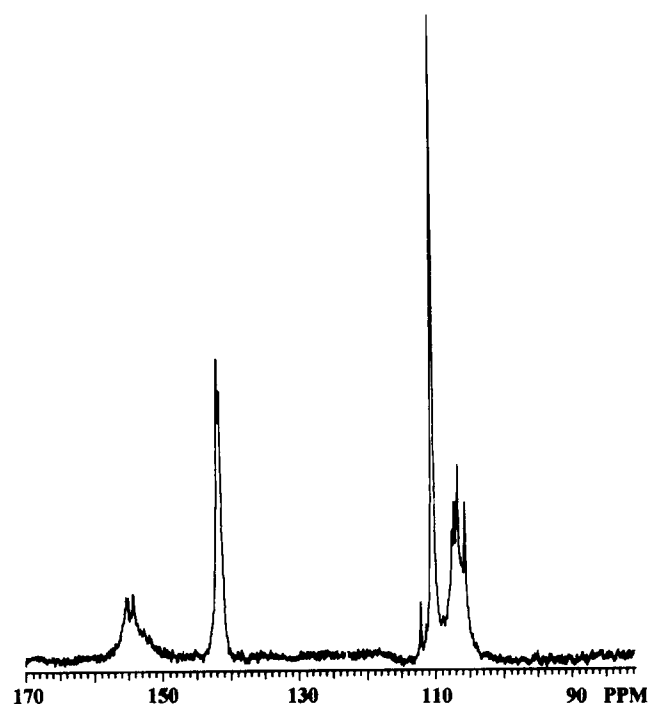

Figure 3 ^{13}C n.m.r. spectrum in CDCl$_3$ solution of PFu.PN.E

Table 3 Electrical properties of neutral and I_2-doped poly(furan)s obtained by $FeCl_3$ in different solvents

Neutral polymer			I_2-doped polymer			
Type	σ $(S cm^{-1})$	E^{*a} (eV)	Type	D^b (mol/mol)	σ $(S cm^{-1})$	E^{*a} (eV)
PFu.Cl.E	$\sim 10^{-13c}$	0.68	PFu.Cl.I	9.8	6.2×10^{-9c}	0.54
PFu.AN.E	$\sim 10^{-13c}$	0.69	PFu.AN.I	9.2	1.8×10^{-9c}	0.56
PFu.PN.E	n.d.^{d}	n.d.^{d}	PFu.PN.I	2.5	n.d.^{d}	n.d.^{d}

^{a} Activation energy of the electrical conductivity
^{b} Molar ratio between neutral and doped units, gravimetrically determined from I_2 uptake, assuming that iodine is present as I_3^- counterion
^{c} Measured on the pressed pellet of the polymer sample
^{d} Film deposited on a glass substrate; n.d. means not determinable

The above data may be also analysed[33] according to equation (1):

$$\sigma = \sigma^0 \exp(-E^*/RT) \qquad (1)$$

where E^* represents the activation energy of the conduction process, T the temperature in K, R the gas-law constant, and σ and σ^0 the conductivities at T and 0 K, respectively. Taking into account that equation (1) may be rearranged as indicated in equation (2):

$$\ln \sigma = \ln \sigma^0 - E^*/RT \qquad (2)$$

the plot of $\ln \sigma$ versus $1/T$ gives rise to a straight line from whose slope E^* can be determined (see for instance *Figure 5* for PFu.Cl.E).

The evaluated E^* data for PFu.Cl.E and PFu.AN.E (*Table 3*) are substantially identical ($\simeq 0.7 eV$) and in agreement with the corresponding data previously reported for undoped poly(furan)s[24].

PFu.CL.E and PFu.AN.E were suspended in an I_2 solution (see Experimental) in order to obtain the corresponding doped polymers PFu.Cl.I and PFu.AN.I. As reported in *Table 3*, the doping level in both systems is substantially the same, a molar ratio (D) between neutral and I_2-doped units of about 9–10 being obtained.

Since in the case of PFu.PN.E the doping carried out in solution gives rise to an insoluble and intractable powder, it was performed by directly exposing the polymeric film to I_2 vapour. In these conditions the I_2

uptake (*Table 3*) is significantly higher than that found for the previous polymers, the obtained PFu.PN.I have a D value of 2.5. which may be related to the much higher content of aromatic units along the polymer backbone. The electroconductivity at room temperature (*Table 3*) of PFu.Cl.I and PFu.AN.I in pressed pellets is very similar ($\sigma \approx 10^{-9} S cm^{-1}$) and about four orders of magnitude higher than that observed for the corresponding neutral polymers. For both materials the current linearly depends on the applied voltage, in the 0–30 V and 20–80°C ranges, thus indicating that they obey Ohm's law and that the contribution of ionic conductivity is also negligible in the doped state. The range of temperature investigated was narrower with respect to that of the corresponding neutral polymers because the I_2-doping is known to be reversible with temperature[31]. Indeed, t.g.a. of PFu.Cl.I clearly shows that a significant weight loss starts to occur over 80°C owing to I_2 evaporation, the consequent decrease of the doping degree causing a reduction of conductivity and hence a deviation from linearity of the current/voltage curves over 80°C. As an example, in *Figure 6* is reported the electrical behavior of PFu.CL.I as a function of temperature.
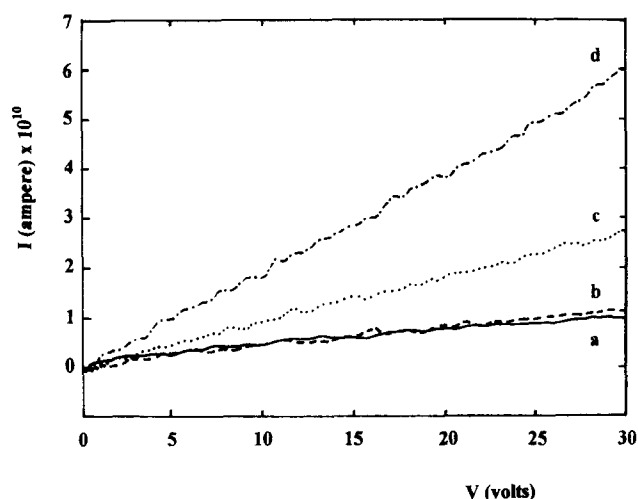
Figure 4 Current intensity versus applied voltage for PFu.Cl.E in a pressed pellet at different temperatures: (a) 72°C; (b) 105°C; (c) 120°C; (d) 170°C
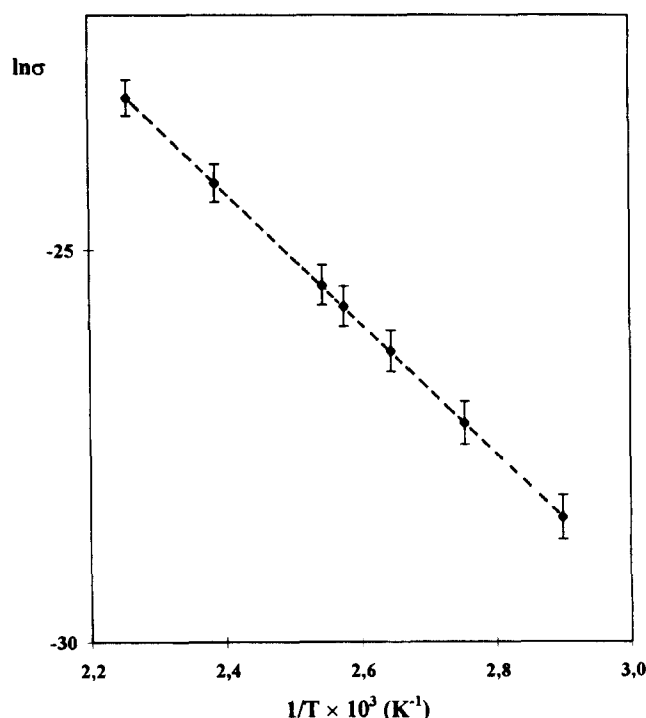
Figure 5 Electrical conductivity $(\ln \sigma)$ versus the reciprocal of temperature $(1/T)$ for PFu.Cl.E in a pressed pellet
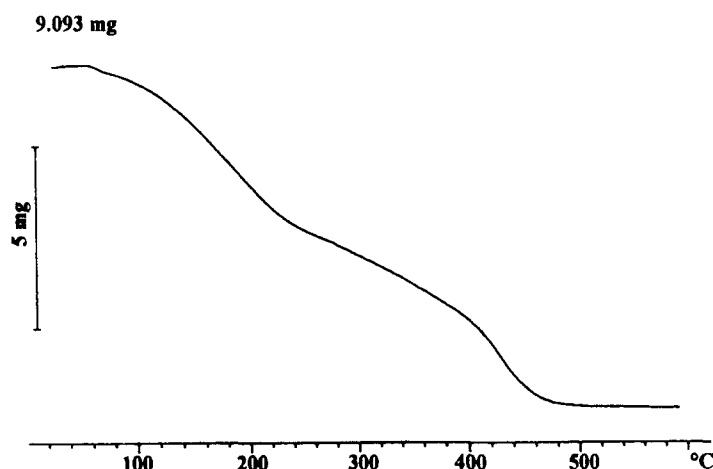
9.093 mg

Figure 6 Thermogravimetric curve for PFu.Cl.I

The activation energies involved in the conductivity process of the I_2-doped polymers (*Table 3*) are very similar (0.54 and 0.56 eV for PFu.Cl.I and PFu.AN.I, respectively). The lower values of E^* in the doped against the neutral polymers allow one to conclude that the I_2-doping not only introduces charge carriers, as shown by conductivity increase, but also modifies their energy distribution.

Unfortunately, electroconductivity measurements carried out on PFu.PN.I in a pressed pellet failed, due to the high brittleness of the sample, probably caused by the too low molecular weight of the polymer. Therefore, it was not possible to compare PFu.PN.I with PFu.Cl.I and PFu.AN.I in terms of σ values on samples equally processed. On the other hand, extreme brittleness and irregular surface morphology did not allow us to measure the electrical conductivity of PFu.PN.I in the film state. Indeed, the microfractures of the film also interrupt the electrical contacts between very close points, and the surface roughness does not allow one to determine, even roughly, the thickness of the film. In order to overcome these problems, the use of polymeric blends consisting of PFu.PN.E and a non-conductive polymer has been explored in order to improve the mechanical properties of the film, in terms of adhesion to the support, plasticity, surface and thickness homogeneity, thus allowing one to measure its conductivity. Moreover, it is well established[34–37] that polymer blends may also improve the resistance to oxidative degradation by the combined action of air, humidity and dopant, thus reducing the ageing of the doped film and hence also

increasing its conductivity stability with time. Therefore, films deposited on glass supports by the spinning technique from solutions of PFu.PN.E and different amounts of a non-conductive polymer, such as poly-(ethylene-*co*-vinyl acetate) (PEVA), were exposed to I_2 vapour. The choice of PEVA, containing 57 mol% of ethylene units, was justified by the fact that a non-conductive polar polymer would give rise to more compatible blends with PFu.PN.E against an apolar polymer, thus affording a material where the conductive component would be more homogeneously dispersed at molecular level and hence able to assure a higher conductivity. As reported in *Table 4*, several PFu.PN.E/PEVA blends, having a weight content of PFu.PN.E in the 5–70 wt % range were tested.

All the films obtained from the above mixtures showed good adhesion to the glass support, homogeneous thickness, smooth surface and improved impact resistance. After I_2 exposure, PFu.PN.I/PEVA films changed colour, becoming dark and brilliant. In all cases the I_2-uptake reached values corresponding to a molar ratio (*D*) between neutral and I_2-doped units equal to 2.2–2.6, substantially identical to that observed for PFu.PN.I alone. In addition, the films after doping were insoluble in the most common solvents, thus suggesting that this treatment causes further oxidative coupling of the oligomeric chains with an extension of the molecular weight and conjugation length.

Electrical properties of the doped films indicate (*Table 4*) that, when the content of PFu.PN.E in the blend is in the 5–15% range, the conductivity is very

Table 4 Electrical conductivity at room temperature of films of PFu.PN.E/PEVA blends after I_2-doping

PFu.PN.E/PEVA				PFu.PN.I/PEVA	
PFu.PN.E (wt%)	Film wt (mg)	I_2-uptake (mg)	D^a (mol/mol)	Thickness (μm)	σ (S cm^{-1})
5	18.0	n.d.^{b}	n.d.^{b}	2.30	$\ll 10^{-5\,c}$
15	20.1	4.8	2.6	3.55	$\ll 10^{-5\,c}$
50	36.2	30.6	2.3	4.95	3.4×10^{-3}
70	45.3	56.8	2.2	5.38	1.3×10^{-2}

^{a} Molar ratio between neutral and doped units
^{b} Not determined
^{c} The value is only indicative and represents the maximum of sensitivity of the instrument
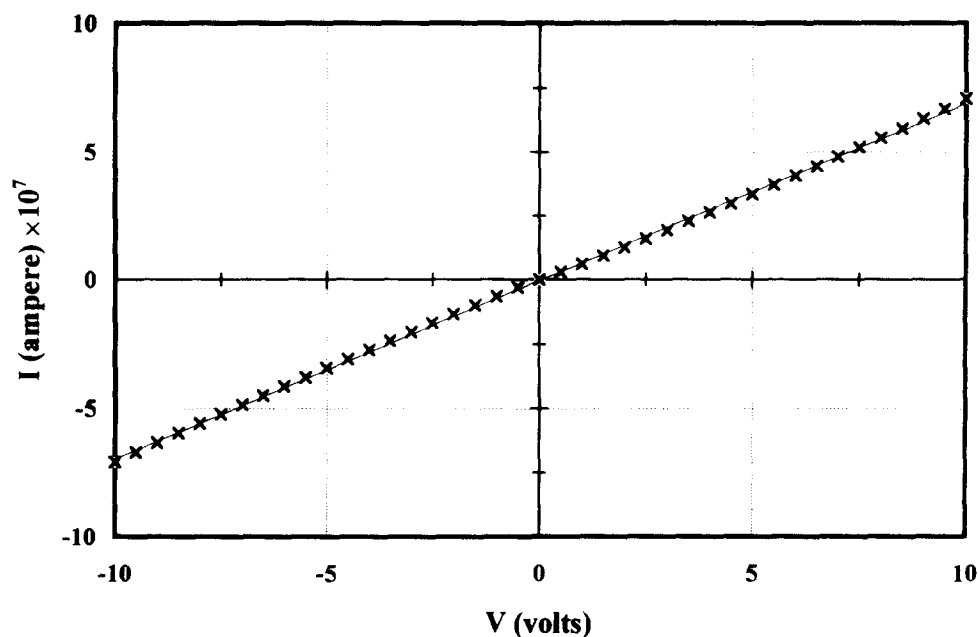
Figure 7 Current intensity *versus* applied voltage for the PFu.PN.I/PEVA (1/1, w/w) blend in the film state

low, but it sharply increases for compositions higher than 50%, reaching for a content of 70% a value of about $10^{-2}\,Scm^{-1}$ at room temperature, seven orders of magnitude higher than that found for PFu.Cl.I and PFu.AN.I. The above data clearly indicate that there is a critical concentration threshold in the blend below which the conductive component domains are not in continuous contact to assure electrical transport, according to the percolation theory[38].

Finally, the linear trend of the current intensity *versus* the applied voltage (*Figure 7*) for the PFu.PN.I/PEVA (1/1) blend confirms also that this type of material has an ohmic behaviour and that no significant contribution of ionic conductivity from the polar PEVA component is present.

CONCLUSIONS

On the basis of the obtained results the following concluding remarks can be drawn.

(1) The oxidative polymerization of furan by $FeCl_3$, $NOBF_4$ and $NOSbF_6$ in aprotic polar media having low donicity affords poly(furan)s with inhomogeneous structure at the molecular level, consisting of randomly distributed aromatic, dihydro- and tetrahydro-furylene as well as 1,4-diketone units. Moreover, the above polymers are, both in the neutral and I_2-doped state, insoluble and non-processable powdery materials having low conductivity.

(2) The use, in combination with $FeCl_3$, of aprotic polar media with high donicity, such as propionitrile, allows one to control the molecular structure of the poly(furan), giving rise to substantially only aromatic units and hence a very highly conjugated main chain. Moreover, in these conditions oligomeric products are obtained, which assures their solubility in the most common organic solvents, both in the pristine and neutral state.

(3) The films obtained from these oligomeric products are, however, too brittle for real applications as

electroconducting materials. Nevertheless, the combination of the above products with proper aprotic polar polymers such as PEVA may afford blends which, after I_2-doping in the film state, display electrical conductivity several orders of magnitude higher than that previously observed for I_2-doped poly(furan)s, thus allowing promising electroconducting materials for real applications to be obtained.

Studies are in progress in order to clarify the mechanism of the oxidative polymerization of furan and 3-substituted furans as well as to optimize the polymerization conditions for increasing the molecular weight of the resulting polymers to such a value to combine solubility of the material with improved mechanical and conductivity properties of the resulting films.

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