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Conjugated polymers bearing furan rings: 1. Synthesis and characterization of oligo(2,5-furylene vinylene) and its thiophene homologue

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A new synthetic route to linear poly(furylene vinylene) is proposed which involves the polycondensation of 5-methylfurfural in a basic medium. This simple one-pot preparation gives low-molecular-weight materials, but with regular linear polymeric structures possessing a high degree of conjugation. The doping of these polymers with iodine gives rise to conductivities of $\sim 1\,\mathrm{S\,cm^{-1}}$. The replacement of the furan ring by the thiophene heterocycle results in a similar behaviour, but with lower reactivity. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(2,5-furylene vinylene); poly(2,5-thienylene vinylene); conjugated structures)

INTRODUCTION

The growing interest in conjugated polymers and oligomers has stimulated the search for novel structures[1], particularly with a view to improving the stability and processability of these materials. Thus, after much research on various parent polymers, such as polyacetylene and polyaniline, heterocyclic moieties were investigated, including polypyrrole and polythiophene. In the last decade, poly(arylene vinylene)s have spurred renewed activity and these structures have been complemented by heteroaromatic analogues. The application of such polymers in electronic, optical and opto-electronic devices is the main driving force behind these investigations[1,2]. Conjugated macromolecules bearing furan heterocycles have received much less attention compared with their sulfur and nitrogen homologues, probably because of their supposedly less-well-defined structures and poor stability. This is, however, a misleading concept as we will try to show in this series of studies. A brief survey of previous work on furanic conjugated polymers is necessary at this point to set the stage.

The cationic polymerization of furan was shown to give rise to complex conjugated oligomers (eventually leading to black insoluble products) in the pioneering work carried out by Wassermann's group[3] in 1967. Little fundamental work has been published since then on the polymerization of furan under the action of added acids or electrochemical initiation[4–7]. Regrettably, the various groups implicated in this research did not attempt to explore in detail the mechanisms of the reactions and the structures involved. It is clear that those polymers had non-linear irregular enchainments which produced crosslinked topologies, but it is likely that a better knowledge of the side reactions occurring in the various systems would have provided a means of improving the quality of the materials. The condensation of furfuryl alcohol promoted by acidic catalysts is accompanied by a complex set of reactions occurring with the oligomers, which generate conjugated sequences made up of alternating furan and dihydrofuran moieties separated by a methine group[8]. These sequences are responsible for the black colour of the products, which are moreover in the form of insoluble networks because of further side reaction and cannot therefore be processed. The cationic polymerization of 2-vinylfurans also leads to conjugated structures in the ensuing polymers by a similar mechanism, but only on terminal segments of the chains, typically involving several monomeric units[9]. These observations related to systems which were not intended to provide conjugated structures emphasize that the presence of furan rings in a polymer can promote the formation of such sequences because of the high lability of the hydrogen atoms which are attached to carbon atoms directly connected to the C(2) and/or C(5) positions of the heterocycle. Thus, structures like polyamides or polyesters in which the furan ring bears carbonyl groups at these positions and with no mobile hydrogen atoms are quite stable and remain colourless even in severe acidic, basic or free-radical media.

The synthesis of poly(2,5-furylene vinylene) (PFV) **1** has been attempted by using different mechanistic approaches, namely: (i) a Wittig-type condensation with the phosphonium salt derived from chloromethylfuraldehyde[10], but in this case no proof was given of the structure claimed for the resulting oligomers; (ii) the self-condensation of 5-methylfuraldehyde in a strongly basic

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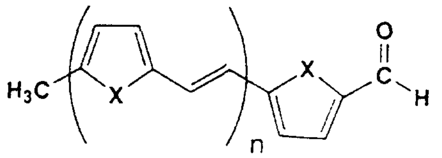
medium[11], which gave black insoluble products for which, again, no convincing evidence was provided to support structure **1**; and (iii) a route simulating the classical synthesis of poly(*p*-phenylene vinylene)s through a soluble precursor[12], with only an infra-red spectrum to characterize the final product.

The modest amount of work published on conjugated furan polymers is in complete contrast to the steady increase in the amount of literature available on homologous aliphatic, aromatic and heteroaromatic structures. Given the large experience of our laboratory in furanic polymers[8], we decided to carry out a detailed investigation aimed at filling that gap.

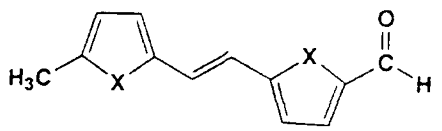
This present paper describes the synthesis and thorough characterization of low-molecular-weight PFV, poly(2,5-thienylene vinylene) (PTV) **2**, and their copolymers. A brief account of some of this work has already been given[1].



polymers

(1) : X = O

(2) : X = S



dimers

(3) : X = O

(4) : X = S

EXPERIMENTAL

Before choosing the synthetic method best adapted to structure **1**, we repeated the polymerizations previously described in the scientific literature, namely routes (ii) and (iii) mentioned above. With the former[11] we obtained the same intractable product, whereas we were not able to reproduce the results reported for the latter[12] because the precursor turned out to be insoluble, despite claims to the contrary, and to yield intractable materials with unclear structures. We decided therefore to concentrate our efforts on the improvement of method (ii) and to tackle the problem from the start by studying the dimerization of 5-methylfuraldehyde (5MF) in various media and with different nucleophiles in order to optimize these synthetic conditions before turning to the actual polymerization.

The most adequate experimental conditions providing access to dimer **3** and to the corresponding oligomers in reasonable yields can be summarized as follows. 10 ml of 5MF were mixed with 10 ml of benzene and 1 g of t-BuOK under magnetic stirring in a nitrogen atmosphere. The resulting mixture was brought to reflux for 3 h. If the reaction was stopped at this point, the major product was dimer **3** in ca. 40% yield. If, on the other hand, a new aliquot of 5MF was added and the reflux maintained, the condensation continued to give oligomers. Successive additions of 5MF (up to 12) at regular intervals, or indeed by a continuous feed with a peristaltic pump, allowed the degree of polymerization (*DP*) to increase progressively. The addition of reagents such as i-Bu_3 Al or CaH_2 further improved both the yields and *DP*s by eliminating the water formed in the condensation reactions. Typical yields for these optimized polymerizations ranged from 70 to 80%.

At the end of each run, the reaction mixture was shaken with water and methylene chloride. The organic phase was dried over sodium sulfate and then concentrated by evaporating about half of the solvent before pouring it into a large excess of methanol. The red-brown solid which precipitated consisted of the higher oligomers, which were isolated by filtration. The filtrate was concentrated in a rotary evaporator in order to remove the solvents. The red viscous liquid obtained was submitted to a high-vacuum distillation at 120°C to separate the dimer from the short-chain oligomers. In one specific experiment this distillation was pursued at a temperature of ca. 200°C in order to collect some trimer for characterization.

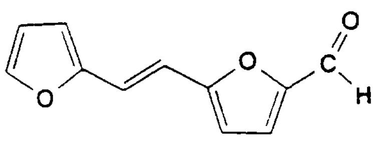
The same experimental procedures were applied to the condensation of 5-methylthiophenecarboxaldehyde (5MT) and to the preparation of its copolymers with 5MF.

The characterization of all of these products called upon the use of elemental analysis, ultra-violet (u.v.)–visible, Fourier transform infra-red (*FT*i.r.), ^{1}H and ^{13}C nuclear magnetic resonance (n.m.r.) spectroscopy, mass spectrometry, vapour pressure osmometry, gel permeation chromatography (g.p.c.), differential scanning calorimetry (d.s.c.) and thermogravimetric analysis (t.g.a.). Electronic conductivities were measured using the four-point technique.

RESULTS AND DISCUSSION

In order to avoid side reactions which introduce structural anomalies and branching points which ultimately lead to crosslinked materials, we limited the nucleophilicity of the medium to the use of a non-polar aprotic solvent and a catalyst of medium strength, and also avoided increasing the reaction temperature above about 80°C. This strategy insured the formation of a linear chain possessing the desired regular structures **1** to **4**.

The specific nature of the various condensation steps involved in the growth of these polymers was investigated in detail. 5MF reacts with a large excess of furfural (avoiding self-dimerization of 5MF) under the conditions described above to give the condensation product **5**:

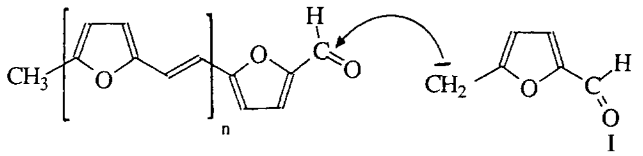


(5)

The characterization of this liquid compound gave the expected mass, and *FT*i.r. and ^{1}H n.m.r. spectroscopic data similar to those detailed in *Table 1* (see below) for dimer **3**, except for the absence of peaks and resonances arising from the methyl group and the presence of the characteristic resonance at 7.6 ppm for the H(5) proton.

This shows that the presence of a methyl group at C(5) is not necessary for the reactivity of the aldehyde moiety. However, 2-methylfuran did not react with furfural or 5MF under the same conditions, which proves that the condensation of methyl groups is only possible if they are attached to a furaldehyde function. This conclusion was confirmed by the fact that 2,5-dimethylfuran was found to be inert towards furfural, 5MF and 2,5-furandicarboxaldehyde, even when more drastic nucleophilic media were tested.

Surprisingly, it turned out that dimer **3** did not condense with itself. In order to assess the reason for this inertness, we studied its reactivity towards furfural and 5MF and found that only the latter gave a trimeric condensation product. This indicates that the methyl group in **3** has lost its reactivity, whereas the carbonyl function maintains the possibility of condensing with the methyl group of 5MF. In conclusion, this condensation reaction, which usually takes place with methyl groups directly attached to carbonyl functions (i.e. the so-called aldol–crotonic condensation), is still possible if the methyl group is attached at the C(2) position of a furan ring bearing a carbonyl function at C(5). However, with the operating conditions chosen for this present study, the methyl group loses its reactivity when the carbonyl group is moved on to a further furan ring, in spite of the conjugation introduced between the two heterocycles. The consequence of this state of affairs is that polymer growth only occurs through successive condensation steps involving the methyl group of the monomer and the aldehyde function of any member of the series, from monomer to polymer:



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These systems are therefore peculiar in that they are polycondensations in terms of the mechanism of monomer attachment to the chain, but polyadditions in their mode of chain growth. A similar behaviour is displayed by the azomethane polymerization catalysed by rare metal atoms to give polymethylene[13,14].

A brief study of the kinetics of the different steps in the growth of the oligomer of 5MF was carried out by measuring the rate of dimerization, trimerization (excess dimer plus 5MF) and oligomerization (excess oligomer plus 5MF). The reactivity of the carbonyl function was found to decrease by a factor of about two when going from monomer to dimer, but to remain essentially the same when comparing dimer and oligomers. Thus, although the qualitative feature is that the carbonyl group remains active, as emphasized above, its reactivity is highest in monomeric 5MF. The activation energy for the dimerization reaction was $25\,\mathrm{kJ\,mol^{-1}}$.

The structural characterization of dimer **3**, oligomers with a *DP* close to 5 and of polymer **1**, having the highest molecular weight attained to date, is summarized in *Table 1*. These data, coupled with the fast atom bombardment (FAB) mass spectra, clearly confirm that the chain growth occurs according to the condensation mechanism I without any appreciable side reactions. In fact, the i.r. and n.m.r. spectra displayed all the characteristic features expected from the 2,5-furylene vinylene unit with the methyl and aldehyde end groups. A typical example is the ^{1}H n.m.r. spectrum of the oligomer shown in *Figure 1*. The multiple peaks for the methyl and aldehyde protons are due to the presence of oligomers with different *DP*s, i.e. different environments for these end-groups. The resonances between 3 and 5.5 ppm arose from traces of solvents used in the work-up of this fraction and not from the product itself. The mass spectrum of dimer **3** gave $M^+ = 202$ and its ^{13}C n.m.r. spectrum was also in excellent accordance with the expected structure. The isolated mixtures of dimer and trimer gave a mass spectrum with both molecular ions present, namely 202 and 294. Whereas the elemental analysis of dimer **3**, which is a yellow crystalline compound (m.p. 86°C), agreed very closely with its calculated composition (C 71.29 instead of 71.28%, H 4.92 instead of 4.98% and O 23.99 instead of 23.74%), those of the various oligomers (viscous liquids to waxy materials) and polymers (brittle solids) tended to show a slightly higher oxygen content than the expected values. We attribute this disagreement to the surface oxidation of these conjugated products. The progressive bathochromic shift and the corresponding widening of the u.v.–visible absorption as a function of the *DP* points to the growing degree of conjugation of these PFVs which

Table 1 Spectroscopic characterization of furanic condensation products

Method	Dimer **3**[a]	Oligomers[b]	Polymer **1**[c]
*FT*i.r.	ν(fur) = 3120, 1591, 1020, 982 and $793\,\mathrm{cm^{-1}}$ $\nu(\mathrm{CH_3}) = 2920\,\mathrm{cm^{-1}}$ $\nu(\mathrm{-C{=}C-}) = 1620$ and $960\,\mathrm{cm^{-1}}$ $\nu(\mathrm{C{=}O}) = 1661\,\mathrm{cm^{-1}}$ $\nu(\mathrm{-CH}) = 2850\,\mathrm{cm^{-1}}$		νfur) = 3115, 1447, 1020 and $783\,\mathrm{cm^{-1}}$ $\nu(\mathrm{CH_3}) = 2920\,\mathrm{cm^{-1}}$ $\nu(\mathrm{-C{=}C-}) = 1651$ and $943\,\mathrm{cm^{-1}}$ $\nu(\mathrm{-CH}) = 2850\,\mathrm{cm^{-1}}$
^{1}H n.m.r.	δ(CHO) = 9.54 ppm, s, $i = 1$ $\delta(\mathrm{CH_3})$ = 2.32 ppm, s, $i = 3$ δ(CH=CH) = 6.78 and 6.73 ppm, $i = 2$ δ(H(fur)) = 6.08, 6.40, 6.48 and 7.21 ppm, $i = 4$		δ(CHO) = 9.54 ppm, weak δ(CH=CH) + δ(Hfur) = 5.8–7.3 ppm $\delta(\mathrm{CH_3})$ = 2.3–2.5 ppm
U.v.–vis	$\lambda_{\max} = 393$ nm; $\epsilon = 4.9 \times 10^4$	$\lambda_{\max} = 430$–490 nm	$\delta_{\max} = 510$ nm, very broad; $\epsilon = 1.6 \times 10^5$

[a] $M = 202$
[b] $M_n = 600$
[c] $M_n = 2000$

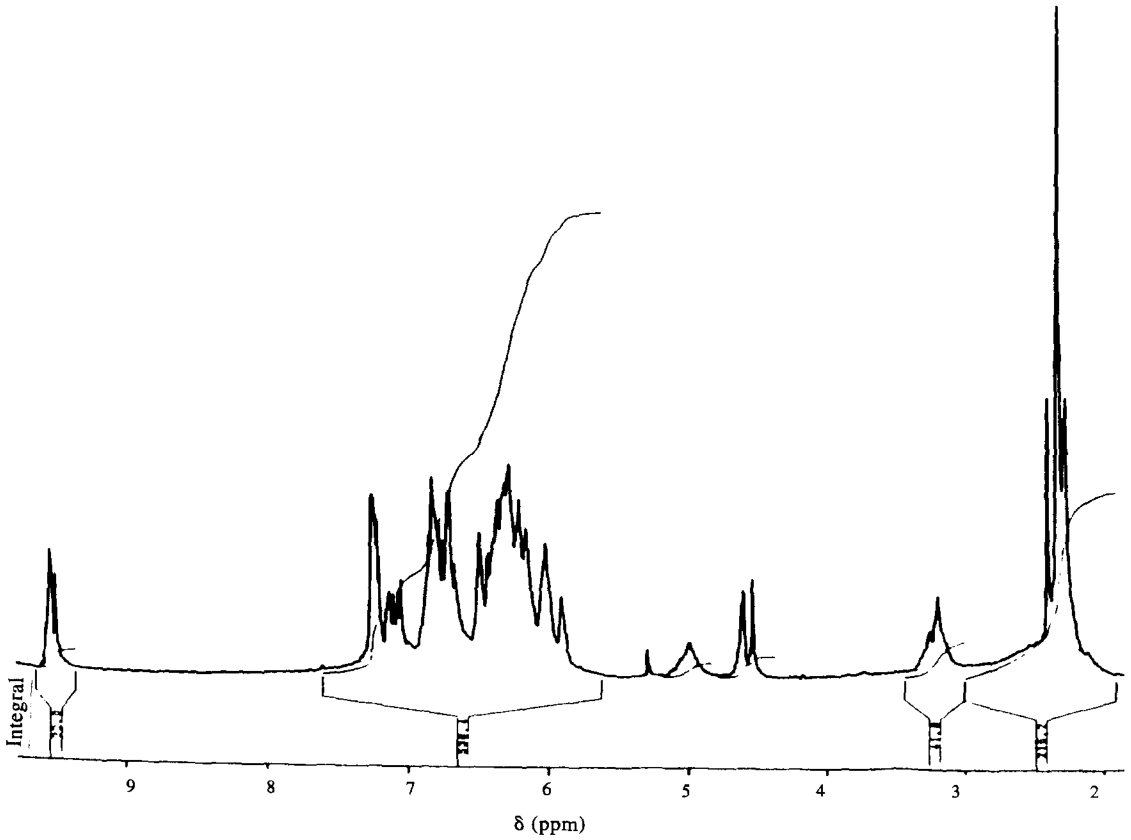


Figure 1 ^{1}H n.m.r. spectrum (CD_2Cl_2) of a typical PFV oligomer

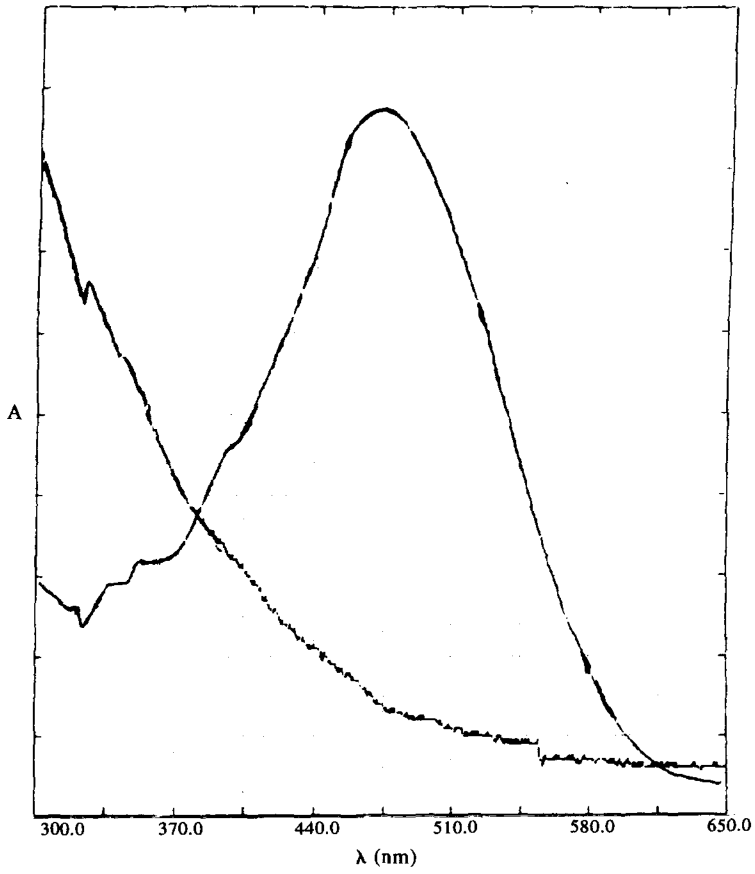
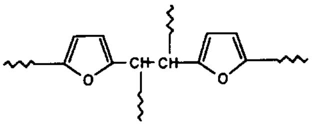
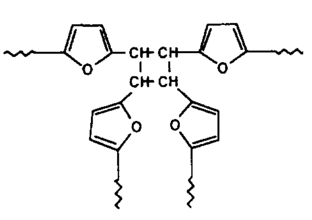


Figure 2 U.v.–vis spectra of PFV before and after irradiation with a medium-pressure Hg lamp

were found to contain mostly *trans*-conformations (coupling constant for the alkene protons of 15 Hz and a typical peak at 960 cm^{-1}). As with other conjugated polymers, a limit in the position of the maximum is attained at relatively low molecular weights[15].

All polymers and oligomers showed a remarkable stability to storage under ambient conditions. In fact no loss of solubility and no detectable changes in the spectra were observed over periods of months. D.s.c. of these dark-coloured polymers showed no clear-cut glass transition and a significant loss of solubility when the temperature was raised above 200°C. It seems likely that the T_gs of these materials are quite high and that condensation reactions inducing branching and finally crosslinking from the initially linear structures occur below their detection. This thermal degradation process seems to take place from the alkenyl moieties since the i.r. spectrum of the insoluble product showed a smaller band at 1650 cm^{-1}, when compared with that of the original polymer. U.v. irradiation of solutions of PFVs in tetrahydrofuran (THF) with a medium-pressure Hg lamp produced a solid precipitate which again showed a decrease in the 1650 cm^{-1} i.r. band and a considerable attenuation of the visible absorption (spectrum from a KBr pellet) indicating a major loss of conjugation, as shown in *Figure 2*. Clearly, the unsaturations between furan rings are involved in both the thermal and the photolytic crosslinking. Two modes of interaction are possible, which would give the following alternative structures:





We have ascertained for both dimer and polymers that the cycloaddition is the dominant photochemical pathway[16]. The furan rings were not involved in these interactions.

The high degree of conjugation of the linear PVFs obtained in this investigation can be further evidenced by the ease of protonation of these structures in solution. In fact the electronic spectra show very large bathochromic shifts, i.e. the addition of triflic acid to methylene chloride solutions related to the dimer **3** moved the λ_{max} from 393 to 527 nm, to the trimer from 430 to 677 nm and to the oligomers and polymers all the way to the near infra-red, namely 900 nm. The obvious implication of this behaviour is the possibility of achieving electronic conductivity from these materials. Pellets of undoped PFVs gave conductivities typical of insulators, i.e. ~10^{-8} S cm^{-1}. Doping with iodine, either from methylene chloride solutions or by vapour deposition, produced a very marked increase in conductivity. *Figure 3* shows the effect of both the extent of doping and of temperature on the conductivity for a PFV of moderate molecular weight. The maximum conductivity was consistently attained for the 'stoichiometric' condition, corresponding to one molecule of iodine per monomer unit, which suggests a specific mode of 1 : 1 doping. Whereas the increase in conductivity with increasing temperature is normal, the subsequent decrease was probably due to the sublimation of iodine out of the polymer. The values of the conductivity are certainly not optimized, mostly because the maximum *DP* attained in our syntheses was still relatively low.

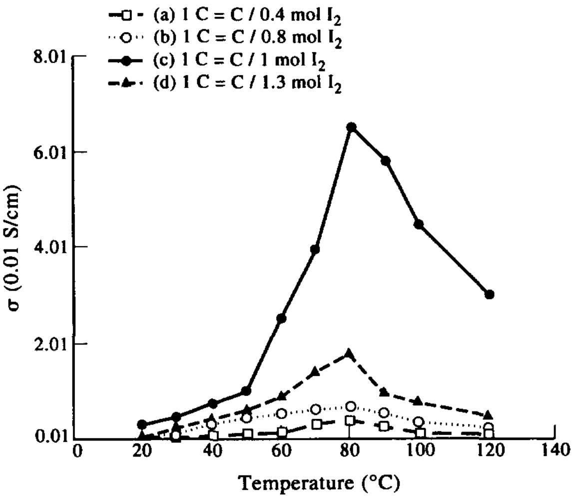


Figure 3 Variation of electronic conductivity of doped PFV as a function of temperature and extent of iodine doping

Table 2 Spectroscopic characterization of thiophenic condensation products

Method	Dimer **4**[a]	Polymer **2**[b]
*FT*i.r.	ν(thio) = 1456, 1433, 1047, 812 and 791 cm^{-1} $\nu(CH_3)$ = 2924 cm^{-1} ν(–C=C–) = 1605 and 947 cm^{-1} ν(–C=O) = 1645 cm^{-1} ν(–CH=) = 2854 cm^{-1}	ν(thio) = 3015, 1516, 1421, 1045 and 800 cm^{-1} $\nu(CH_3)$ = 2920 cm^{-1} ν(–C=C–) = 1605 and 933 cm^{-1} ν(–C=O) = 1657 cm^{-1}
^{1}H n.m.r.	δ(CHO) = 9.8 ppm, s, $i = 1$ $\delta(CH_3)$ = 2.48 ppm, s, $i = 3$ δ(CH=CH) = 6.70 and 6.87 ppm, $i = 2$ δ(H fur) = 6.95, 7.09, 7.24 and 7.85 ppm, $i = 4$	δ(CHO) = 9.7 ppm δ(CH=CH) + δ(H = thio) = 6.63–7.20 ppm $\delta(CH_3)$ = 2.5 ppm
U.v.–vis	λ_{max} = 390 nm	λ_{max} = 465 nm

[a] $M = 234$
[b] $M_n = 1400$

Table 3 Spectroscopic characterization of furanic–thiophenic mixed condensation products

Method	Oligomers[a]	Polymer[b]
*FT*i.r.	ν(fur) = 3130, 1533, 1020 and 719 cm^{-1}	ν(fur) = 3117, 1508, 1020 and 783 cm^{-1}
	ν(thio) = 3060, 1433 and 791 cm^{-1}	ν(thio) = 3055 and 1427 cm^{-1}
	ν(CH=O) = 1657 cm^{-1}	ν(CH=O) = 1659 cm^{-1}
	ν(CH=CH) = 1630 and 945 cm^{-1}	ν(CH=CH) = 1608 and 939 cm^{-1}
	ν(CH_3) = 2922 and 2854 cm^{-1}	ν(CH_3) = 2922 and 2854 cm^{-1}
^{1}H n.m.r.	δ(CH_3) = 2.2–2.6 ppm	δ(CH_3) = 2.25 ppm
	δ(H thio, fur, CH=CH) = 6–7.8 ppm	δ(H thio, fur, CH=CH) = 6–7.6 ppm
	δ(CH=O) = 9.6 ppm	δ(CH=O) = 9.6 ppm
U.v.–vis	λ = 415 and 295 nm	λ = 510 nm

[a] Elemental analysis: calc. C 72, H 4, O 8, S 16%; found C 61, H5, O 19, S 13%
[b] Elemental analysis: calc. C 72, H 4, O 8, S 16%; found C 69, H 4, O 18, S 8%

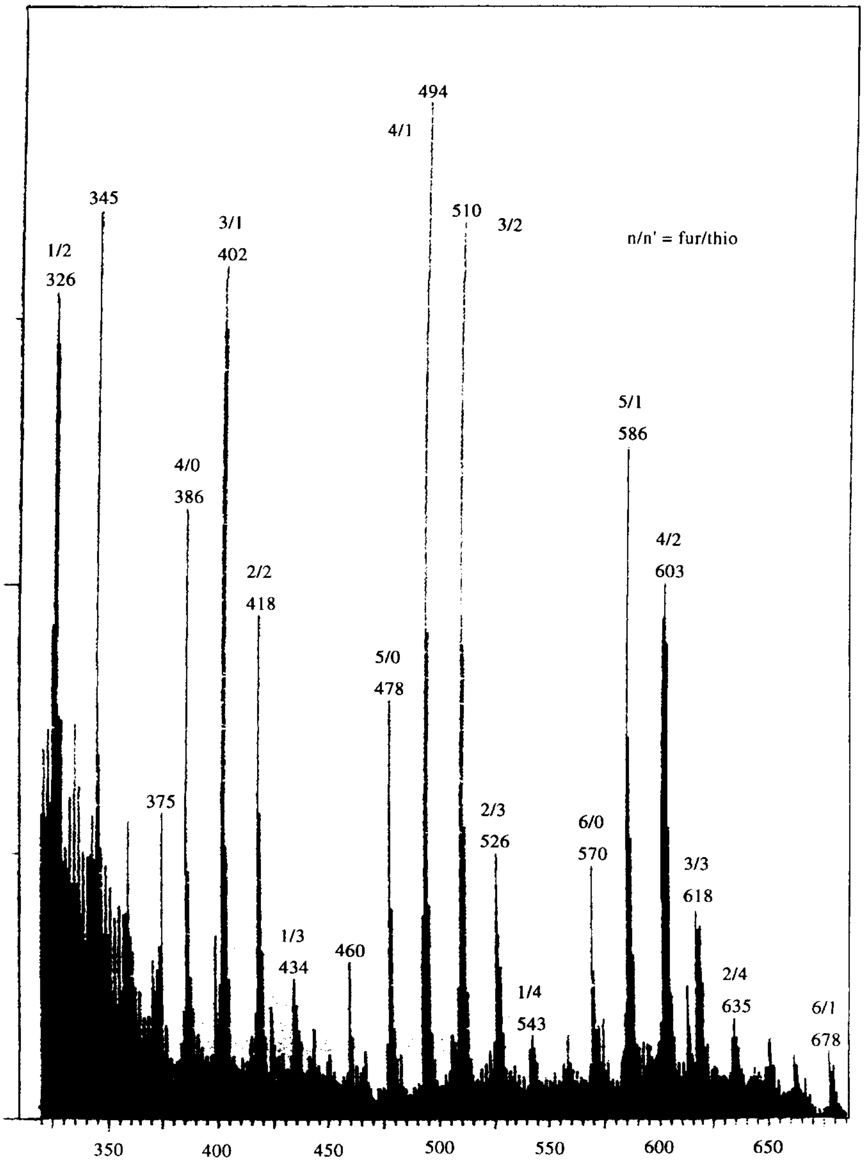


Figure 4 Mass spectrum of a typical random PFV–PTV copolymer

This did not hinder the conduction, which obviously took place by interchain propagation given the low *DP*s of these materials, but it is likely that at least an increase by an order of magnitude can be obtained with higher molecular weights and also perhaps by using other dopants.

The particularly simple one-pot preparation of linear PFVs described in this study was applied to the thiophene homologues. 5-Methylthiophenecarboxaldehyde behaved qualitatively like 5MF and the resulting products were isolated and characterized accordingly. *Table 2* gives their spectroscopic features. Again, all analytical indications, which included mass spectra and elemental analyses, pointed to regular structures **2** and **4** without any detectable anomalies. Dimer **4** (m.p. 95°C) gave C 61.22 instead of a calculated content of 61.54%, H 4.61 instead of 4.21%, O 6.58 instead of 6.83% and S 27.25 instead of 27.35%. Quantitatively, the condensation reactions were slower and led to lower molecular weights. Thus, the value of λ_{max} of the polymer which had only reached $M_n = 1400$ was considerably lower than the corresponding value for PFV with $M_n = 2000$, due to the lesser degree of conjugation. The reason for this diminished reactivity is probably related to the stronger aromatic character of the thiophene heterocycle, compared with the more dienic properties of the furan ring. Indeed, attempts to provoke the self-condensation of 4-methylbenzaldehyde (and also of the 2- and 3-isomers) failed under our mild conditions, with the starting compounds being recovered quantitatively. On the basis of these considerations, it would be expected that 5-methyl-*N*-methylpyrrolcarboxaldehyde should readily react to give the corresponding poly(2,5-*N*-methylpyrrolene vinylene) since pyrrole has a dienic/aromatic character which is intermediate between those of furan and thiophene. However, this aldehyde did not display any reactivity under our typical conditions, a failure for which we have no explanation at present. Other heteroaromatic methyl aldehydes which failed to react were 3-methyl-2-thiophenecarboxaldehyde and *N*-methyl-2-pyrrolcarboxaldehyde. The probable reasons for these failures is the lack of reactivity of the methyl group when it is not in the C(5) position, and/or problems of steric hindrance.

Having established that both furan and thiophene derivatives were reactive, albeit with different kinetics, we examined the behaviour of systems in which the two aldehydes were introduced simultaneously into the reaction medium. The products were isolated according to the usual procedure and *Table 3* gives the spectroscopic properties of these random co-oligomers and copolymers in which the presence of both heterocycles were clearly detected. *Figure 4* shows the FAB mass spectrum of a sample of this type of co-oligomer. The presence of molecular peaks corresponding to a number of uniform and mixed structures is the major feature of this spectrum: thus the mixed structures n/n' (number of furanic to number of thiophenic units) 1/2, 3/1, 2/1, 1/3, 4/1, 3/2, etc., are clearly visible together with dimers, trimers, etc. arising from homocondensations. The elemental analysis of both oligomers and polymers gave systematically a large excess of oxygen to the detriment of the sulfur content, compared with the calculated value based on an equal consumption of each monomer in the copolycondensation. These results confirm the difference in reactivity observed in the two homopolycondensations, emphasized here by the higher incorporation of the furan monomer.

Block copolymerizations were also carried out by adding the thiophene monomer at the end of a polymerization reaction involving 5MF. The spectroscopic features of these products were completely similar to those reported in *Table 3*, but the mass spectra showed a much higher extent of uniform sequences, which were longer for the furan units. The elemental analyses confirmed the higher reactivity of the furanic monomer. The extent of blocking was not determined and work is in progress in this context.

CONCLUSIONS

The new synthetic route developed in this investigation is particularly interesting for its simplicity and for the advantage of providing regular linear heteroaromatic-vinylene structures. Two drawbacks persist, however, namely the low molecular weight of the polymers that are obtained and their consequent poor mechanical properties. In fact the films cast from these PFVs were brittle and no fibres could be spun. The further pursuit of this work aims to improve these aspects and to extend the range of performances of the various materials, e.g. in photoactivity, electroluminescence and non-linear optics.

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