

Synthesis and characterization of alkyl-substituted poly(thiophene-2,5-diylvinylene)s

A. Bolognesi*, M. Catellani, W. Porzio and F. Speroni

Istituto di Chimica delle Macromolecole, CNR, Via Bassini 15, 20133 Milano, Italy

and R. Galarini, A. Musco and R. Pontellini

Istituto di Scienze Chimiche, Università di Urbino, 61129 Urbino, Italy

(Received 2 June 1992; revised 11 December 1992)

A new synthetic route for the preparation of poly(thiophene-2,5-diylvinylene)s consisting of the C–C coupling reaction of alkyl-substituted 2,5-diiodothiophene and *E*-1,2-bis(tri-*n*-butylstannyl)ethylene catalysed by palladium complexes is described. The resulting polymers are soluble. These materials have been extensively characterized by Fourier-transform infra-red and ^{13}C nuclear magnetic resonance spectroscopy. The optical properties have been examined. The polymers are deep blue in the neutral state and transparent in the doped state. The solid-state structure of these materials will be discussed according to X-ray diffraction data.

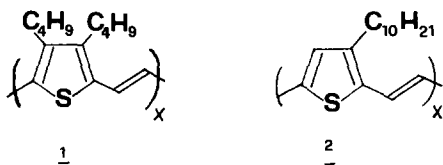
(Keywords: poly(thiophene-2,5-diylvinylene)s; alkyl substituent; synthesis; characterization)

INTRODUCTION

Great attention has recently been devoted to poly(arene-diylvinylene)s owing to their interesting electro-optical properties¹. By alternating thiophene rings and vinylene groups in the polymeric backbone, a lowering of the band gap with respect to polythiophene is produced.

Two different routes have been proposed previously for the synthesis of these materials. One method consists of the preparation of a precursor polymer, which is then thermally treated to yield the polyconjugated chain^{1,2}. The other method consists of the Ni-catalysed coupling reaction of an arene di-Grignard derivative and 1,2-dihaloethylenes^{3,4}.

We have recently reported⁵ that poly(thiophene-2,5-diylvinylene)s are conveniently prepared by the coupling reaction of 2,5-diiodothiophene and *E*-1,2-bis(tri-*n*-butylstannyl)ethylene catalysed by Pd complexes. Full experimental details are reported here for the preparation of poly(3,4-dibutylthiophene-2,5-diylvinylene) (**1**) and poly(3-decylthiophene-2,5-diylvinylene) (**2**) as well as an extensive spectroscopic investigation of these materials.



EXPERIMENTAL

All the preparations were carried out under nitrogen purified by passage through R3-11 BASF catalyst.

* To whom correspondence should be addressed

Materials

1,1'-Bis(diphenylphosphino)ferrocene and HSnBu_3 were Aldrich products. $(\eta^3\text{-2-Methylallyl PdOAc})_2$ was prepared by reacting $(\eta^3\text{-2-methylallyl PdCl})_2$ with stoichiometric amounts of TIOAc in CH_2Cl_2 . *E*-1,2-Bis(tri-*n*-butylstannyl)ethylene⁶ and alkyl-2,5-diiodothiophene^{7,8} were prepared according to the literature. *N,N*-Dimethylformamide (DMF) was distilled from CaH_2 prior to use.

Elemental analyses were performed in the following laboratories: (i) Mikroanalytisches Labor Pascher, Remagen-Bandorf, Germany; (ii) Redox, Milano; and (iii) Microanalysis Laboratory, Department of Organic Chemistry, University of Milano.

Poly(3,4-dibutylthiophene-2,5-diylvinylene) (**1**)

3,4-Dibutyl-2,5-diiodothiophene (0.896 g, 2.0 mmol) and *E*-1,2-bis(tri-*n*-butylstannyl)ethylene (1.21 g, 2.0 mmol) were added to a DMF solution (20 ml) of $(\eta^3\text{-C}_4\text{H}_7\text{PdOAc})_2$ (0.011 g, 0.025 mmol) and 1,1'-bis(diphenylphosphino)ferrocene (0.111 g, 0.20 mmol). The mixture was refluxed for 10 h. After cooling to room temperature, the resulting black solid material was isolated by centrifugation of the reaction mixture. The solid was washed with DMF, methanol and then with hexane to give (**1**) (0.183 g, 47%) as a black powder. Difficulties were experienced in performing the elemental analysis of the isolated material. The analytical determinations carried out in different laboratories gave different values. The lack of reproducibility is likely to be due to the difficult combustion of the samples. Accordingly, an abundant black uncombusted residue was observed. Elemental analysis calculated for $-(\text{C}_{14}\text{H}_{20}\text{S})_x-$: C 76.36%, H 9.09%, S 14.54%. Found: (i) C 66.22%, H 7.75%, S 9.78%.

I 0.13%, Sn 3.08%; (ii) C 50.73%, H 6.11%, S 8.40%, I 2.38%; (iii) C 69.77%, H 8.45%.

Poly(3-decylthiophene-2,5-diylvinylene) (2)

This was similarly prepared (35% yield). Elemental analysis calculated for $-(C_{16}H_{24}S)_x-$: C 77.41%, H 9.67%, S 13.02%. Found: (i) C 63.71%, H 7.85%, S 7.69%, I 0.13%, Sn 6.72%; (ii) C 64.25%, H 7.84%, S 9.40%, I 1.30%; (iii) C 64.54%, H 7.90%. The 1H n.m.r. spectrum shows three peaks in the aromatic region due to the vinyl and thiophene protons ($\delta = 6.80, 6.91, 6.94$ ppm). The peak at $\delta = 2.62$ ppm is attributed to the CH_2 in the α position with respect to the thiophene ring.

Polymers **1** and **2** are soluble in chloroform, tetrahydrofuran (THF) and partially in DMF, and can be cast on glass, on quartz or on ITO (indium tin oxide) glass to give thin polymeric films. G.p.c. data (Table 1) are referred to standard polystyrene and were obtained with a Waters 600E instrument using chloroform as solvent. As the tributyltin group is present in some chains (see elemental analysis) it may influence the value of the molecular weight. We believe that this influence is very small because the g.p.c. technique is sensitive to the overall size of the macromolecules and the volume of the tributyltin group is not big in comparison to that of the macromolecules bearing them. However, our view is that the obtained molecular weights are not absolute values; rather, they give a trend of the molecular weight within a series of polymerizations of the same monomer without giving a true indication of the value. X.r.d. spectra were carried out with a computer-controlled Siemens D-500 diffractometer for unoriented samples, using graphite-monochromated Cu $K\alpha$ radiation, Soller slits and a scintillation counter.

Ultra-violet/visible/near-infra-red (u.v.-vis.-n.i.r.) absorptions were measured with a Varian Cary 2400 instrument and FT.i.r. spectra were recorded on a Bruker IFS 66 instrument on cast film deposited on KBr pellets at room temperature (resolution 2 cm^{-1}).

Electrochemical doping was performed in a quartz cell containing a solution of tetrabutylammonium perchlorate in acetonitrile. A thin polymeric film on ITO glass was the cell anode, a platinum wire being the cathode. The doping of the polymers was performed by applying a constant current of 0.1 mA cm^{-2} . Chemical doping of the polymers was performed in dry chloroform solution by addition of iodine under nitrogen atmosphere.

Thermochromism of the polymers was studied by heating thin films deposited on quartz with a Mettler FP5 and FP21 temperature controller while recording the electronic absorption spectra. N.m.r. spectra were registered on a Bruker AC-200 instrument. ^{13}C n.m.r. spectra were assigned by d.e.p.t. (distortionless enhancement by polarization transfer) experiments.

Table 1 G.p.c. data of **1** and **2**

Polymer ^a	M_w	M_w/M_n
1	3600	1.3
1	4200	1.5
2	8600	1.6
2	8700	1.6

^aThe data are referred to samples prepared in different runs

Degradation experiments on polymers **1** and **2** were performed by exposing the chloroform solution of the polymers to a u.v. laboratory lamp ($= 254\text{ nm}$) for 10 min at the distance of 10 cm. Samples for FT.i.r. measurements were cast on KBr windows from these solutions.

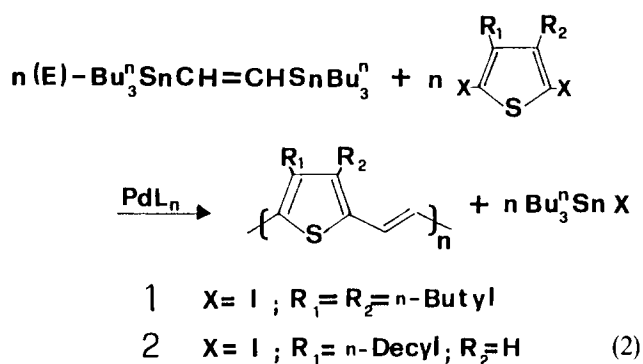
RESULTS AND DISCUSSION

Polymerization

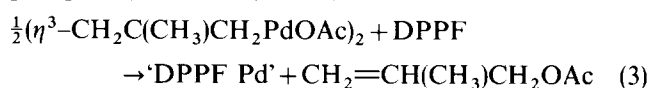
The coupling reaction of aryl electrophiles and tin organometallics catalysed by Pd complexes (equation (1)) following the pioneering work by Stille⁹ has found wide application in synthetic organic chemistry for C-C bond formation:



We have found that Stille's reaction may be extended to the preparation of poly(thiophene-2,5-diylvinylene)s by reacting 2,5-dihalothiophene with E-1,2-bis(tri-*n*-butylstannyl)ethylene according to:



The reaction is conveniently run in boiling DMF. The catalytically active Pd(0) species is prepared in the reaction medium from $(\eta^3\text{-C}_4\text{H}_7\text{PdOAc})_2$ and the appropriate phosphorus ligand, i.e. 1,1'-bis(diphenylphosphino)ferrocene (DPPF):



The peculiar properties of DPPF in C-C bond formation have been remarked upon by several authors¹⁰.

N.m.r. analysis

The microstructures of the polymers were established by ^{13}C n.m.r. The assignment of the resonances of **1** is straightforward (Figure 1). The spectrum of **2** is complex owing to the irregular head-to-tail sequence of the thiophene unit in the polymer backbone (Figure 2). The resonances centred at 120 ppm are assigned to vinyl carbon atoms by comparison with the chemical shift of a model compound (E-3,3'-dimethyl-2,2'-dithienylethylene, $\delta = 119.5$ ppm). The number of peaks, four, is that expected for the expected sequences: head-to-head (HH), one resonance; head-to-tail (HT) (tail-to-head, TH), two resonances; tail-to-tail (TT), one resonance (Figure 3). Through d.e.p.t. experiments the resonances centred at $\delta = 142, 140, 137$ ppm were assigned to substituted thiophene carbons, while that at $\delta = 130$ ppm to unsubstituted ring carbon.

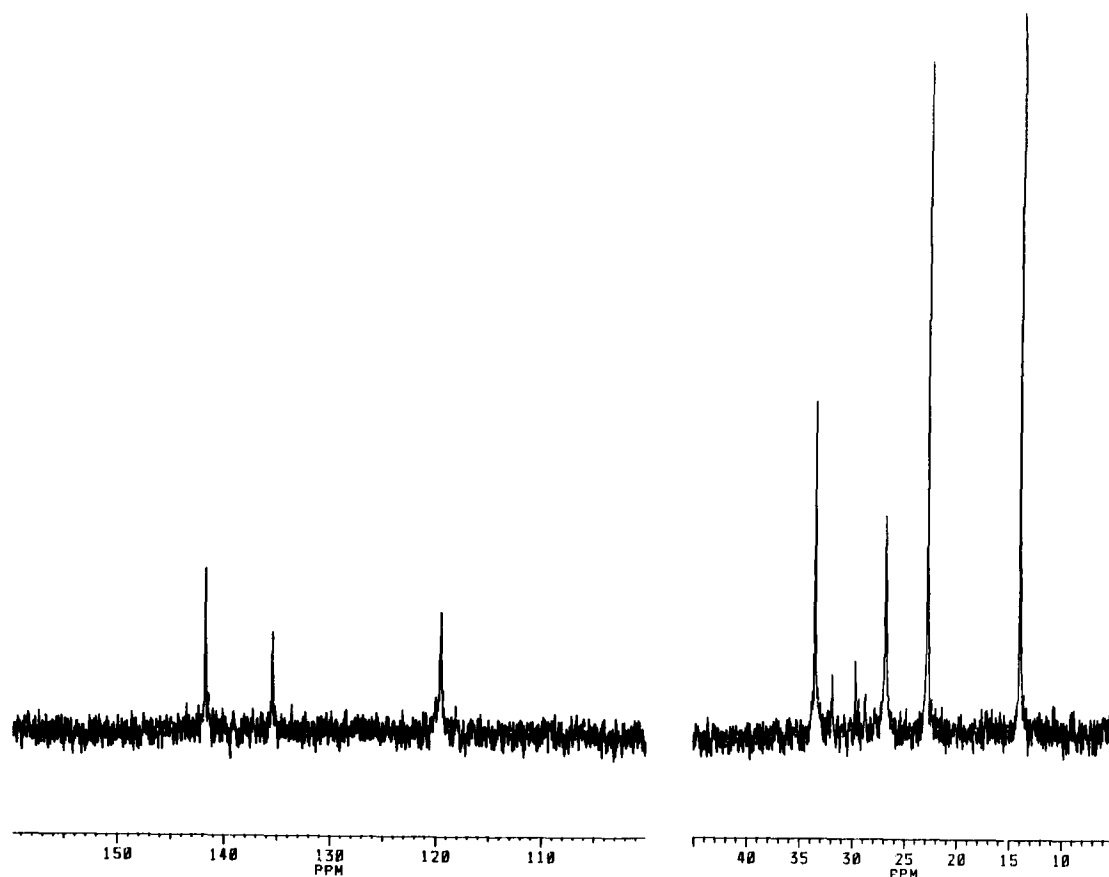


Figure 1 ^{13}C n.m.r. of 1: $\delta = 13.9$ ppm, $\text{CH}_3(\text{CH}_2)_2\text{CH}_2-$; $\delta = 22.8$ and 26.8 ppm, $\text{CH}_3(\text{CH}_2)_2\text{CH}_2-$; $\delta = 33.5$ ppm, $\text{CH}_3(\text{CH}_2)_2\text{CH}_2-$; $\delta = 119.5$ ppm, $=\text{CH}-$; $\delta = 135.3$ and 141.6 ppm, carbons of the aromatic ring

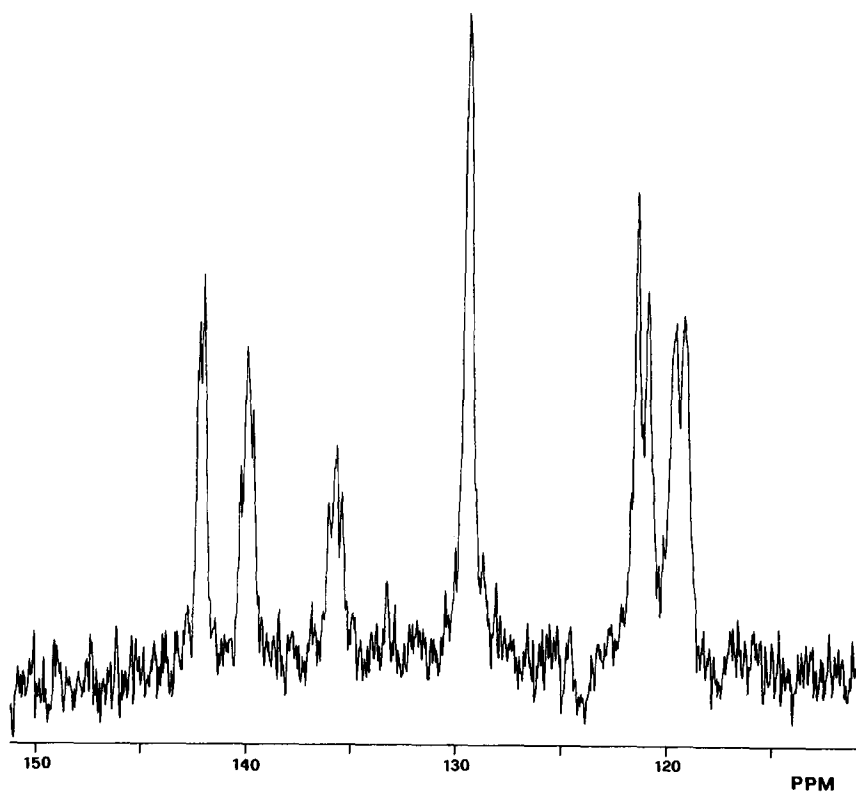


Figure 2 ^{13}C n.m.r. of 2: peaks centred at $\delta = 142$, 140 and 137 ppm were assigned to substituted thiophene carbons; peak at $\delta = 130$ ppm to unsubstituted ring carbon. For assignment of peak at $\delta = 130$ ppm, see text

FTi.r. analysis

In Figures 4a and 4b the spectra of polymers 1 and 2 are reported respectively. The *trans* geometry of the double bond was confirmed by the presence of the band at 919 cm^{-1} (1) and at 922 cm^{-1} (2) due to the out-of-plane bending of the C-H bond in a *trans* configuration¹¹. In the model compound E-1,2-(3,4,3'4'-tetra-n-butyl-2,2'-dithienyl)ethylene this vibration mode was observed at 932 cm^{-1} . In Table 2 the more relevant absorptions for the two polymers are reported together with their assignments.

Chloroform solutions of 1 and 2 are sensitive to the combined action of oxygen and light. Films cast from chloroform solutions irradiated as described in the experimental part display strong absorption bands due to oxidation products (1262 , 1102 , 1024 , 802 cm^{-1} and 1260 , 1098 , 1024 , 804 cm^{-1} for 1 and 2 respectively) and simultaneously decreasing intensity of the vinylene vibration mode. A shift towards higher frequencies is observed for the out-of-plane C-H bending of 1 and 2 (from 919 to 928 cm^{-1} and from 922 to 929 cm^{-1} respectively), indicating an overall decrease of the conjugation length (see for comparison the frequency of

the same vibrational mode in the model compound E-1,2-(3,4,3'4'-tetra-n-butyl-2,2'-dithienyl)ethylene).

U.v.-vis. spectra

The u.v.-vis. spectrum of cast film of 2 shows the absorption of the $\pi-\pi^*$ transition with a maximum at 605 nm . The band gap calculated from this optical transition is about 1.80 eV . The chloroform solution of 2 shows an electronic absorption with the maximum at 578 nm and an E_g at 1.85 eV . Polymer 1 has a band gap at 1.70 eV in the solid state, while the band gap in chloroform solution is 1.95 eV . Polymer 1 as well as 2 were electrochemically doped on ITO glass electrodes by applying a low current density for different times. The *in situ* electronic absorption spectra of 1 have been recorded for various doping levels; the visible spectral region is reported in Figure 5. Neutral 1 has a strong absorption band with a maximum at 550 nm assigned to $\pi-\pi^*$ transition that decreases with increasing doping level. The maximum variation in absorbance at 550 nm (green region of the spectrum) is 75% . This strong electrochromic effect between the neutral and the doped polymer is reversible with doping–dedoping processes for at least 10 cycles. Polymer 1 is blue and quite transparent

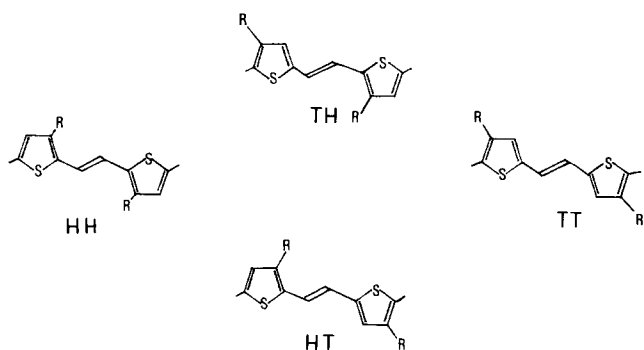


Figure 3 Expected sequences in the polymer chain of 2

Table 2 FTi.r. data of 1 and 2^a

1	2
3015 $\nu(\text{CH vin})$	3062 $\nu(\text{CH ring})$
2954 $\nu_a(\text{CH}_3)$	3015 $\nu(\text{CH vin})$
2928 $\nu_a(\text{CH}_2)$	2952 $\nu_a(\text{CH}_3)$
2867 $\nu_s(\text{CH}_3)$	2921 $\nu_a(\text{CH}_2)$
2858 $\nu_s(\text{CH}_2)$	2851 $\nu_s(\text{CH}_2)$
	1464 $\delta(\text{CH}_2 \text{ in plane})$
	1436 $\delta(\text{C=C ring})$
919 $\delta(\text{CH vin op})$	922 $\delta(\text{CH vin op})$
	830 $\delta(\text{CH ring op})$

^a op = out of plane; vin = vinylene

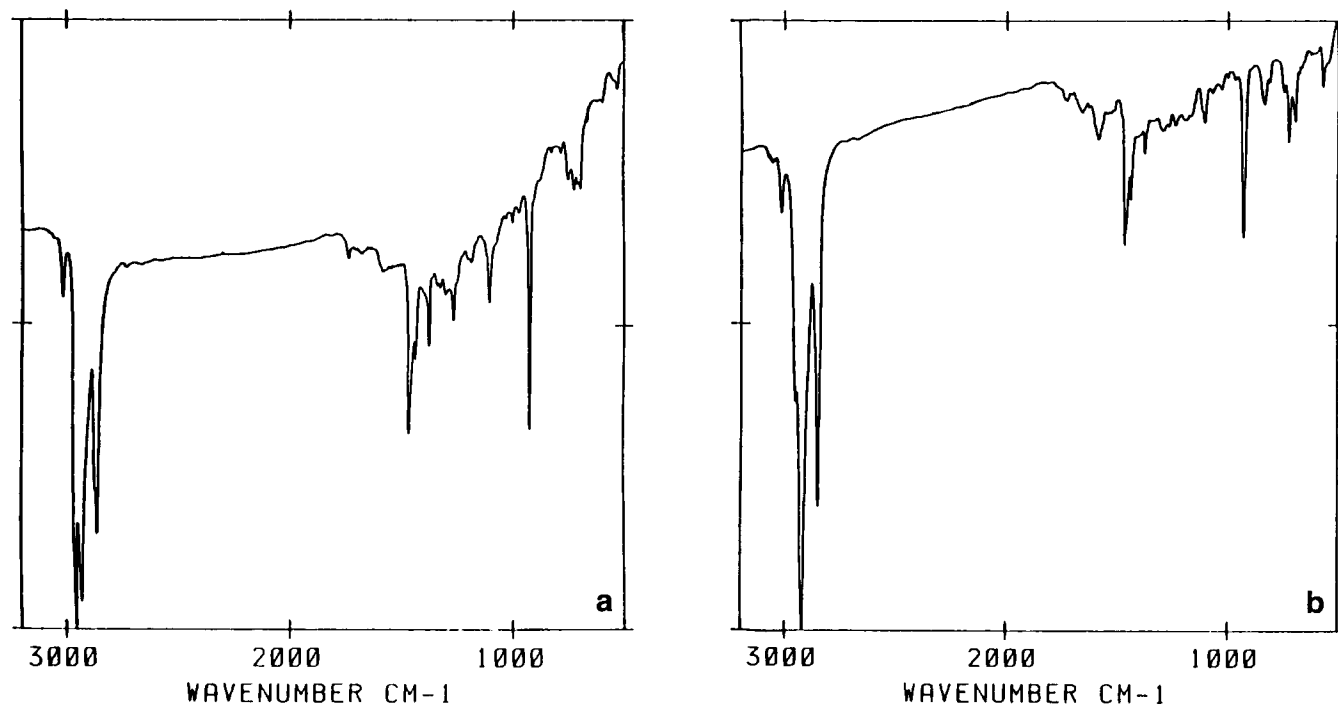


Figure 4 FTi.r. spectra of 1 (a) and 2 (b)

in the neutral and oxidized state respectively. An iodine chemical doping of **1** has been performed in chloroform solution. The evolution of u.v.-vis.-n.i.r. absorptions was followed during the process. When the polymer solution is doped the absorbance of the $\pi-\pi^*$ band decreases while its maximum (2.1 eV) is shifted to higher energy. Two broad peaks characteristic of the oxidized state and centred at 1.05 and 0.69 eV appear, as shown in *Figure 6*. This behaviour is commonly observed for conjugated polymers with a non-degenerated ground state¹² and the two bands due to the doping can be interpreted as bipolaronic species formation.

The thermochromic behaviour of both polymers was followed in the solid state. *Figure 7* shows the electronic absorption spectra of cast film of polymer **1**. The maximum of the absorption peak shifts towards higher energy with increasing temperature, producing a change in polymer colour from blue to red-blue (550 to 515 nm). The corresponding absorption edge of the band gap, on the contrary, does not shift remarkably, this behaviour being very similar to that of the poly(3-alkylthiophene)s series¹³.

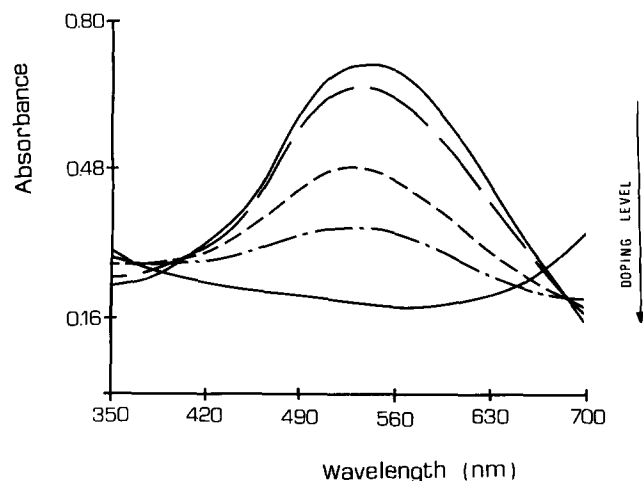


Figure 5 Variation of the absorbance of **1** in the visible spectral region at different doping levels

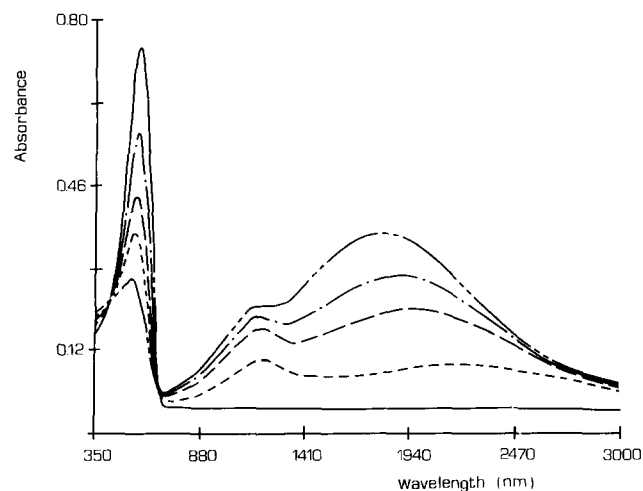


Figure 6 U.v.-vis.-n.i.r. spectra of **1** in chloroform. The addition of different amounts of iodine to a solution of neutral polymer (full curve) produces the doping of the polymer (dashed curves)

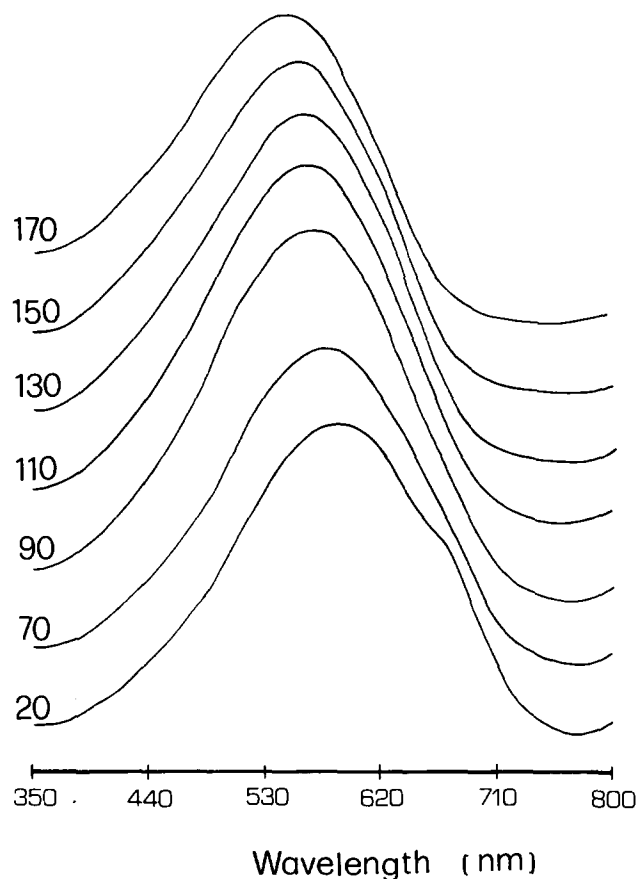


Figure 7 Temperature dependence of absorption spectrum of **1** film (temperature (°C) is shown on each curve)

Conductivity

Conductivity data for both **1** and **2** (I_2 doped) were in the range of $10^{-2} \text{ S cm}^{-1}$. The presence of the tri-*n*-butylstannyl group as chain end seems to have no effect on the conductivity data. In fact, undoped polymer, still containing traces of tin as detected by elemental analysis, is an insulator ($\sigma = 10^{-10} \text{ S cm}^{-1}$).

X-ray analysis

X.r.d. spectra of **1** and **2** are reported in *Figure 8* together with that of unsubstituted poly(thiophene-2,5-diylvinylene) (PTV)¹. We note the presence of relevant amorphous part in the polymers, no diffraction effects over 33° (i.e. 2.71 \AA) and a shift of the maximum spacing as a function of side-chain length. Similar observations were found in the poly(alkylthienylene) series (PAT) for which a consistent model was proposed¹⁴. In analogy with this system we may derive a possible 3D arrangement for **1** and **2** by assuming a planar main chain (imposed by 2_1 symmetry axis) constituted by alternating thienylene rings linked by *trans*-vinylene moieties giving a reliable chain repeat of 12.9 \AA . We extended this model to the other terms of the series considering side chains near to *trans* conformations. In *Table 3* the *d*-spacings for **1**, **2** and PTV are reported.

It is worth mentioning that, owing to the poor x.r.d. patterns shown in *Figure 8*, the proposed model should be considered as tentative, and therefore we were able to derive a unit cell for unsubstituted PTV only. Inferring a primitive monoclinic cell, we derived: $a = 7.67 \text{ \AA}$, $b = 4.68 \text{ \AA}$, $c = 12.90 \text{ \AA}$, $\gamma = 92.3^\circ$, $d(\text{calc}) = 1.56 \text{ g cm}^{-3}$ to be compared with a flotation value of 1.59 g cm^{-3} .

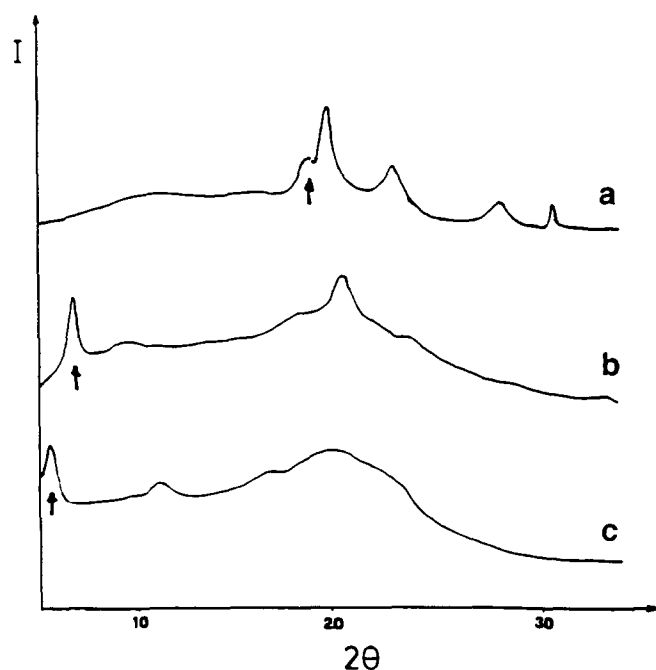


Figure 8 X.r.d. patterns of PATV series: PTV (a), **1** (b), **2** (c). The arrows indicate the longest d -spacings

Table 3 Poly(thiophene-2,5-diylvinylene) series d -spacings (Å)

PTV	5.59, 4.65, 4.44, 3.84, 3.08
1	13.0, 9.07, 4.81, 4.32, 3.64
2	16.06, 8.03, 4.4

For both poly(thiophene-2,5-diylvinylene) and PAT series we observed a linear trend of the longest d -spacings as a function of carbon atom number of the side chains, as already found in comb-like macromolecular systems¹⁵. Specifically we observed shorter long spacings in

poly(thiophene-2,5-diylvinylene)s than in the PAT series, irrespective of side-chain length, suggesting a more effective alkyl chain interdigitation for the poly(thiophene-2,5-diylvinylene) system.

ACKNOWLEDGEMENTS

The authors thank Mr A. Schieronni for g.p.c. measurements. This work was partially supported by Progetto Finalizzato Materiali per Tecnologie Avanzate of CNR.

REFERENCES

- 1 Yen, K. Y., Han, C. C. and Elsenbaumer, R. L. *Mol. Cryst. Liq. Cryst.* 1990, **186**, 211
- 2 Murata, H., Tokito, S., Tsutsui, T. and Saito, S. *Synth. Met.* 1991, **36**, 95
- 3 Yen, K. Y., Eckart, H., Jon, T. R., Shacklette, L. W. and Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* 1988, 215
- 4 Van Dort, P. C., Pickett, J. E. and Blohm, M. L. *Synth. Met.* 1991, **42**, 2305
- 5 Galarini, R., Musco, A., Pontellini, R., Bolognesi, A., Catellani, M., Destri, S., Mascherpa, M. and Zhou, G. *J. Chem. Soc., Chem. Commun.* 1991, 394
- 6 Bottaro, J. C., Hansan, R. H. and Seitz, D. E. *J. Org. Chem.* 1981, **46**, 5221
- 7 Tamao, K., Kodama, S., Nakajima, I., Kumada, M., Minato, A. and Suzuki, K. *Tetrahedron* 1982, **38**, 3347
- 8 Barker, J. M., Huddleston, P. R. and Wood, M. L. *Synth. Commun.* 1975, **5**, 59
- 9 Stille, J. K. *Angew. Chem., Int. Edn. Engl.* 1986, **25**, 508
- 10 Hayashi, T., Konishi, M., Kumada, M., Higuchi, T. and Hirotsu, K. *J. Am. Chem. Soc.* 1984, **106**, 158
- 11 Furukawa, Y., Sakamoto, A. and Tasumi, M. *J. Phys. Chem.* 1989, **93**, 5354
- 12 Heeger, A. J., Kivelson, S., Schrieffer, J. R. and Su, W. P. *Rev. Mod. Phys.* 1988, **60**, 781
- 13 Yoshini, K., Nakajima, S., Onoda, M. and Sugimoto, R. *Synth. Met.* 1989, **28**, C349
- 14 Bolognesi, A., Catellani, M., Destri, S., Mascherpa, M., Musco, A. and Porzio, W. in 'Materials for Photonics Devices' (Eds. A. D'Andrea, A. Lapicciarella, G. Marletta and S. Viticoli), World Scientific, Singapore, 1991, p. 303
- 15 Magagnini, P. L. *Makromol. Chem. Suppl.* 1981, **4**, 223