

New Electrogenenerated Conducting Poly(thiophenes) containing Substituted Phenyl Groups

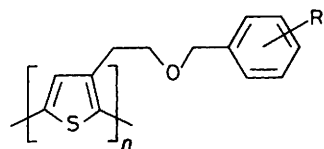
Jean Roncali,^{*a} Hafsa Korri Youssoufi,^a Robert Garreau,^b Francis Garnier,^a and Marc Lemaire^b

^a Laboratoire des Matériaux Moléculaires, CNRS ER 241, 2 rue Henry Dunant, 94320 Thiais, France

^b Laboratoire de Chimie Organique, UA 1103, CNAM, 292 rue Saint-Martin, 75003 Paris, France

New conducting polymers have been synthesised by electropolymerisation of 3-(benzyloxyethyl)thiophenes; substitution of the phenyl ring has no direct electronic effect on the conjugated backbone but controls the spectroscopic and electrochemical properties of the polymer by means of substituent interactions.

Conducting polymers obtained by electropolymerisation of modified thiophene monomers have recently attracted much attention. Thus it has been shown that the 3-substitution of thiophene by alkyl, alkyl sulphonate, or polyether chains considerably increases the solubility of poly(thiophene).¹ More recently, it was shown that the electropolymerisation of



- (1) unsubstituted
- (2) R = *p*-F
- (3) R = *p*-CF₃
- (4) R = 2,3,4,5,6-F₅

thiophenes substituted in the 3-position by chiral,² redox,³ or oxyalkyl groups⁴ leads to functional conducting polymers with specific electrochemical properties.

The structural basis for the grafting of phenyl groups on poly(thiophene) has already been analysed and the need for a spacer between the thiophene ring and the phenyl group to minimize the steric hindrance to conjugation has been demonstrated.⁵ Taking this conclusion into account, we report here preliminary results on a new series of poly(thiophenes) (PTs) (1)–(4) in which substituted phenyl groups are linked to the thiophene ring *via* an oxyethyl spacer.

It is shown that, whereas the substitution of the phenyl ring has no direct electronic effect on the conjugated backbone, the interactions between the substituted phenyl groups exert a strong effect on the spectroscopic and electrochemical properties of the polymers.

The synthesis and characterisation of the monomers have

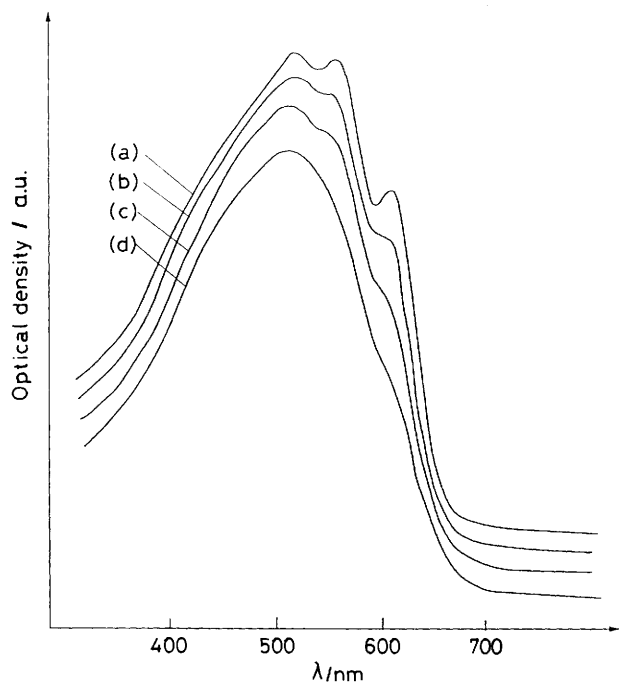


Figure 1. Absorption spectra of undoped poly(1)–(4), deposition charge 50 mC cm^{-2} on ITO. (a) (2), (b) (1), (c) (3), (d) (4).

Table 1. Electrochemical data for polymers (1)–(4) (E in V).

Polymer	p Doping				n Doping		
	E_{pa}^1	E_{pa}^2	E_{pc}	y_p (%)	E_{pa}	E_{pc}	y_n (%)
(1)	0.56	0.82	0.75	20	-1.84	-1.94	9.5
(2)	0.54	0.82	0.75	18	-1.80	-1.91	12
(3)	0.54	0.80	0.75	17	-1.84	-1.97	7.7
(4)	0.55	0.90	0.86	20	No 'n' doping		

been described elsewhere.⁶ Electropolymerisations were carried out in nitrobenzene containing the monomer (0.2 mol l^{-1}) and Bu_4NPF_6 (0.02 mol l^{-1}), using established procedures.⁷ Films for electrochemical characterisation were grown on Pt disk electrodes ($s = 7 \times 10^{-2} \text{ cm}^2$), electrochemically undoped and placed in dry acetonitrile containing LiClO_4 or Et_4NClO_4 (0.1 mol l^{-1}). All potentials refer to the saturated calomel electrode (SCE). UV-visible absorption spectra and conductivities were obtained on films grown on indium-tin oxide (ITO) coated glass. A deposition charge of 1 C cm^{-2} led to free-standing films of $5\text{--}7 \mu\text{m}$ thickness with a four-probe conductivity (σ) of $5\text{--}10 \text{ S cm}^{-1}$. Limiting the film thickness to $0.5 \mu\text{m}$ increased σ to $20\text{--}25 \text{ S cm}^{-1}$ as previously observed for other substituted PTs.^{4,8}

Figure 1 shows the electronic absorption spectra of the undoped polymers. In each case the absorption maximum (λ_{max}) occurs at *ca.* 520 nm, similar to that for poly(3-alkylthiophenes) with long alkyl chains (P3ATs).⁷ These results confirm that, when connected to the thiophene ring by a spacer of appropriate length, the phenyl group induces no distortion of the polymer backbone and hence no steric hindrance to conjugation.⁵ Furthermore, this invariance of λ_{max} shows that the substitution of the phenyl ring exerts no inductive or field electronic effect on the conjugated backbone.

The spectrum of (2) exhibits a fine structure, with a maximum at 518 nm and two well defined side bands at 556

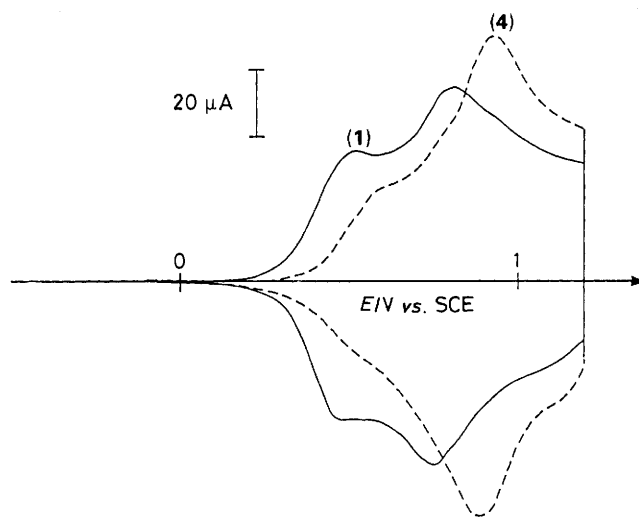


Figure 2. Cyclic voltammograms of (1) and (4) in MeCN containing LiClO_4 (0.1 mol l^{-1}). Deposition charge 100 mC cm^{-2} on Pt, scan rate 50 mV s^{-1} .

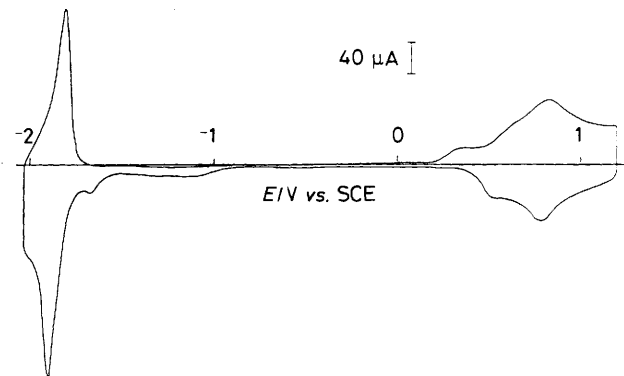


Figure 3. Cyclic voltammogram of (2) in MeCN containing Et_4NClO_4 (0.1 mol l^{-1}). Deposition charge 100 mC cm^{-2} on Pt, scan rate 100 mV s^{-1} .

and 608 nm. These absorption features appear also in the spectra of (1), (3), and (4), but the intensity of the fine structure bands decreases in the order (2) > (1) > (3) > (4). Absorption shoulders at analogous wavelengths have previously been observed in the low-temperature spectra of P3ATs and it has been shown that they correspond to vibronic transitions involving C=C bond stretching in the thiophene ring.^{9,10} Since vibronic structure was not observed in the spectrum of unsubstituted PT, it was proposed that the ordering effect resulting from the interactions between the alkyl chains is a necessary condition for the vibronic structure to be observed.¹⁰ On the basis of this conclusion, the enhancement of vibronic structure observed in the room-temperature spectrum of (2) compared to the low-temperature spectra of P3ATs films¹⁰ suggests that in (2) stronger substituent interactions lead to an ordering effect which is larger at room temperature than that obtained at low temperature for P3ATs. Accordingly, the progressive disappearance of fine structure from (2) to (4) suggests that the substitution of the phenyl ring modifies the interactions between the pendant substituents, thus disturbing the ordering effect associated with these interactions.

Figure 2 shows the cyclic voltammograms (CV) of (1) and (4) in LiClO_4 . The CVs of (1), (2), and (3) are similar and show two successive anodic waves at *ca.* 0.5 V (E_{pa^1}) and 0.80 V (E_{pa^2}), as already observed for other substituted PTs.^{4,7,8} In the case of (4), the intensity of the first wave decreases and E_{pa^2} occurs at a potential *ca.* 100 mV more anodic. Table 1 shows that the p doping level (y_p) (determined from the amount of charge exchanged upon redox cycling) lies in every case in the region of 20%, indicating that the substitution of the phenyl ring has little effect on the electroactivity related to p doping. Attempts to achieve an electrochemical n doping by Li^+ were unsuccessful while in the presence of Et_4N^+ a sharp symmetrical redox system corresponding to the cation doping/undoping process was observed at -1.90 V (Figure 3). Preliminary stability tests have shown that (2) retains more than 95% of its initial electroactivity after 50 cycles between 0 and -2 V. The highest n doping level (y_n) of 12% was achieved with (2); y_n then decreases for (1) and (3), and (4) could not be n doped (Table 1). These results show that, in contrast to p doping, the n doping process depends strongly on the substitution of the phenyl ring.

Since the four polymers show similar conjugation lengths and y_p values, the strong differences in their y_n values and the fact that these values are correlated with the intensity of the vibronic structure suggest that the p and n doped states have different geometries and that the structural reorganisation associated with the n doping process requires a more ordered polymer structure than the p doping. This hypothesis appears consistent with the recent demonstration that poly(3-methylthiophene) can be n doped at low temperature.¹¹

To summarise, highly conjugated poly(thiophenes) containing substituted phenyl groups have been synthesised. We have shown that, although the substitution of the phenyl ring has no direct electronic effect on the conjugated system, it exerts a

determining effect on the spectroscopic and electrochemical properties of the polymers through substituent interactions.

Received, 26th September 1989; Com. 9/04132J

References

- 1 M. Sato, S. Tanaka, and K. Kaeriyama, *J. Chem. Soc., Chem. Commun.*, 1986, 873; K. Jen, G. G. Miller, and R. L. Elsenbaumer, *ibid.*, 1986, 1346; A. O. Patil, Y. Ikenone, F. Wudl, and A. J. Heeger, *J. Am. Chem. Soc.*, 1987, **109**, 1858; M. R. Bryce, A. Chissel, P. Kathirgamanathan, D. Parker, and N. M. R. Smith, *J. Chem. Soc., Chem. Commun.*, 1987, 466; M. Feldhues, G. Kämpf, H. Litterer, T. Mecklenburg, and P. Wegener, *Synth. Metals*, 1989, **28**, C487.
- 2 M. Lemaire, D. Delabouglise, R. Garreau, A. Guy, and J. Roncali, *J. Chem. Soc., Chem. Commun.*, 1988, 658; D. Kotkar, V. Joshi, and K. Gosh, *ibid.*, 1988, 917.
- 3 R. Mirrazaei, D. Parker, and H. S. Munro, *Synth. Metals*, 1988, **30**, 265.
- 4 J. Roncali, R. Garreau, D. Delabouglise, F. Garnier, and M. Lemaire, *J. Chem. Soc., Chem. Commun.*, 1989, 679.
- 5 J. Roncali, R. Garreau, D. Delabouglise, F. Garnier, and M. Lemaire, *Synth. Metals*, 1989, **28**, C341.
- 6 M. Lemaire, R. Garreau, H. Korri Youssoufi, and J. Roncali, *New J. Chem.*, submitted for publication.
- 7 J. Roncali, R. Garreau, A. Yassar, P. Marque, F. Garnier, and M. Lemaire, *J. Phys. Chem.*, 1987, **91**, 6706.
- 8 J. Roncali, A. Yassar, and F. Garnier, *J. Chem. Soc., Chem. Commun.*, 1988, 581.
- 9 S. D. D. V. Rughooputh, S. Hotta, A. J. Heeger, and F. Wudl, *J. Polym. Sci.*, 1987, **25**, 1071.
- 10 M. Sundberg, O. Inganäs, S. Stafström, G. Gustafsson, and B. Sjögren, *Solid State Commun.*, 1989, **71**, 435.
- 11 R. M. Crooks, O. M. R. Chyan, and M. S. Wrighton, *Chem. Materials*, 1989, **1**, 2.