New soluble poly(2-methoxy-5-alkoxy paraphenylenes). Electrosynthesis and spectroscopic characterization

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Polymers of 1-methoxy-4-ethoxybenzene (PMEP), 1-methoxy-4-n-hexoxybenzene (PMHP) and 1-methoxy-4-[2-(1-adamantyl)-2-oxo-ethoxy]benzene (PMAP) were electrosynthesized in 0.1 M tetrabutylammonium tetrafluoroborate acetonitrile solution and characterized. While PMEP is practically insoluble, PMHP and PMAP are soluble in usual organic solvents such as methylene chloride, chloroform, carbon tetrachloride, tetrahydrofuran and dimethylformamide. Structural characterization using Fourier transform infra-red and nuclear magnetic resonance spectroscopy indicates that these polymers have a linear and well-defined polymeric structure. Gel permeation chromatography studies show number average molecular weights between 2200 and 2900 with degrees of polymerization between 10 and 11 for PMHP and PMAP. Electrical conductivities range between 2×10^{-5} S cm^{-1} and 2×10^{-2} S cm^{-1} for PMEP, PMHP and PMAP in the oxidized state. Ultraviolet absorption, excitation and emission fluorescence spectra were measured for the polymers in solution and for solid films. The red shift ($\simeq$0.70 eV) of the fluorescence emission maximum of the polymers (peak at $\sim$3.10 eV) relative to the monomers is discussed in terms of π-electron delocalization and excimer formation.The Stokes shift is consistent with the presence of two exciton–polaron levels for polymers in solution.

(**Keywords: spectroscopy; conducting polymers; characterization**)

INTRODUCTION

Electronically conducting polymers have been a subject of great interest during the last decade. Indeed, numerous potential applications can be expected from their good thermal and oxidative stabilities, their electrical conductivity (generally between 10^{-4} S cm^{-1} and 10^{2} S cm^{-1}) and their flexibility, which is needed for thin layer deposition on different substrates[1]. Several types of organic polymers, including polyacetylenes, polyanilines, polyparaphenylenes, polythiophenes and polypyrroles have been synthesized by various chemical, photochemical and electrochemical methods[2]. However, most of these materials are essentially insoluble in organic solvents, which constitutes a serious drawback for industrial applications. Attempts have been made recently to enhance the solubility and processibility of polythiophenes and polyparaphenylenes by substituting the heteroaromatic or aromatic ring with polar groups and/or flexible side chains[3–10]. The solubility of 3-alkylthiophene polymers in organic solvents was first reported by Elsenbaumer *et al.*[5] and Sato *et al.*[6]. The Heeger group processed electrochemically conjugated poly(3-alkylthienylenes) from chloroform solution, used them as semiconducting and metallic polymers, and studied their spectroscopic properties[3]. The neutron scattering properties of these compounds were also studied by Aime *et al.*[4]. Bryce *et al.*[7] found that highly conductive (10^{3} S cm^{-1}) and soluble polymers could be prepared from β-substituted thiophenes. Very recently, Ruiz *et al.*[8] chemically synthesized and characterized ethylmercapto-substituted polythiophenes that are soluble in common organic solvents such as methylene chloride, chloroform and tetrahydrofuran (THF). However, these materials are insoluble in more polar solvents, such as methanol, acetone and water. Yamamoto *et al.*[9] reported the electrochemical preparation of poly (2,5-dimethoxy-1,4 phenylene) which was characterized by infra-red (i.r.) and solid-state ^{13}C nuclear magnetic resonance (n.m.r.) but this polymer is partially soluble only in concentrated sulphuric acid. Similar results were obtained by Le Berre *et al.*[10] who also discussed the mechanism of electropolymerization of paradimethoxybenzene. Very recently, Renahn *et al.*[11] described the chemical synthesis of poly(p-2,5-di-n-alkylphenylene)s via the Yamomoto route and palladium catalysed coupling of 4-bromo-2,5-di-n-hexylbenzene boronic acid. These polymers, with degrees of polymerization (DP) ranging between 13 and $\sim$30 according to the preparation route used, were claimed to be soluble in several organic solvents such as chloroform, methylene chloride and toluene[11]. This solubility was attributed by the authors to the presence of a long, flexible alkyl side chain.

In this paper, we report on the electrosynthesis and spectral characterization of three new poly(2-methoxy-5-alkoxy-1,4-phenylenes) (PMAP). We investigated the effect of varying the structure of the alkoxy group on the solubility and spectroscopic properties of this type of polymer.

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EXPERIMENTAL

Preparation of monomers

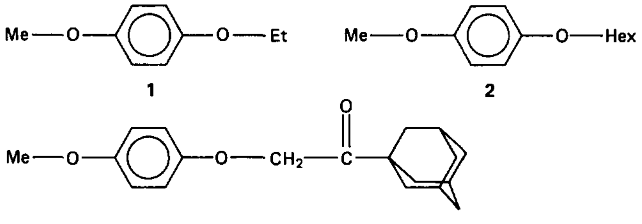
1-Methoxy-4-ethoxybenzene (MEB) (**1**) and 1-methoxy-4-n-hexoxybenzene (MHB) (**2**) (*Scheme 1*) were prepared by alkylation of 4-methoxyphenol using the method of Fiala[12]. Equimolar amounts of 4-methoxyphenol and ethyl (or n-hexyl) iodide were refluxed in ethanol at boiling point, in the presence of potassium t-butylate. Recrystallization from ethanol yielded white crystals of **1** (m.p. 36°C, lit. 39°C) and **2** (melting at room temperature).

1-Methoxy-4-[2-(1-adamantyl)-2-oxo-ethoxy]benzene (MAB) (**3**) (*Scheme 1*) was prepared by three alkylation procedures which were recently described[13]. In procedure A, equimolar amounts of 1-adamantyl-1-bromomethylketone and triethylamine were refluxed with 4-methoxyphenol in dry acetone for 5 h. In procedures B and C the alkylation was performed, respectively, by solid–liquid and liquid–liquid phase transfer catalysis (PTC) (*Scheme 2*).

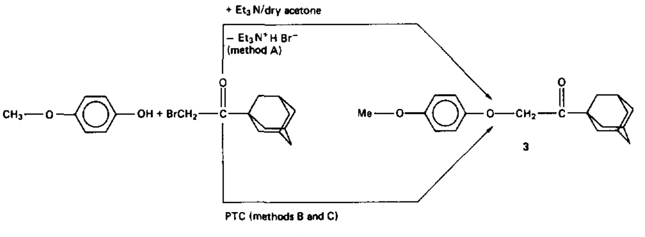
After recrystallization from petroleum ether, compound **3** was obtained as colourless crystals [m.p. 96°C; yield 73% (A), 71% (B), 98% (C)]. Analysis calculated for $C_{19}H_{24}O_3$: C, 76.00; H, 8.00. Found: C, 75.75; H, 8.05. I.r. (KBr) $\bar{\nu}$ (cm^{-1}) 2901 (adamantyl), 1706 (C=O). ^1H n.m.r. (DMSO-d_6) δ (ppm) 1.69–1.98 (15H, adamantyl), 3.68 (s, 3H, CH_3), 4.94 (2H, CH_2), 6.80 (4H, aromatic).

Electrosynthesis of polymers

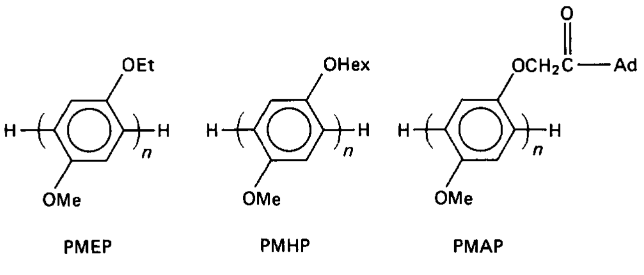
Poly(2-methoxy-5-ethoxy paraphenylene) (PMEP), poly(2-methoxy-5-hexoxy paraphenylene) (PMHP) and poly{2-methoxy-5[2-(1-adamantyl)-2-oxo-ethoxy]paraphenylene} (PMAP) (*Scheme 3*) were electrosynthesized by electrochemical oxidation of 1×10^{-2} M of the corresponding monomers in 0.1 M tetrabutylammonium tetrafluoroborate ($TBABF_4$) dry acetonitrile solution. The electrochemical cell has been described previously[14]. The solution was degassed by bubbling dry argon, and it was maintained under a slight argon overpressure.



Scheme 1



Scheme 2



Scheme 3

A PAR model 273 potentiostat-galvanostat equipped with a Sefram model TGM 164 X–Y recorder was utilized for the electropolymerization. The working electrode was a thin, rectangular glass slide coated with a 500 nm thick platinum layer deposited by cathodic sputtering using a Blazers Sputron II with a platinum target (Balzers purity 99.9%). The reference electrode was an Ag wire with chemically coated AgCl. The auxiliary electrode was similar to the working electrode.

Electrosynthesis of polymers was performed at a controlled, constant potential (1.8 V *versus* Ag/AgCl). To obtain sizeable amounts of polymers, this procedure was repeated four to five times in several acetonitrile solutions. Then the samples were gathered and the polymers were purified by evaporation of the solvent, dissolution in chloroform, filtration, reprecipitation into methanol and dried under vacuum.

Spectral characterization

Infra-red spectra of monomers and polymers were obtained by using a Nicolet S-60 Fourier transform infra-red spectrophotometer. Pressed KBr pellets were utilized. Ultraviolet (u.v.) absorption spectra were performed either in solution or on ITO electrodes (2–10 $\Omega\, cm^{-2}$, CNET Laboratory, Lannion, France), by means of a Varian DMS-200 u.v.–visible spectrophotometer. ^{13}C n.m.r. spectra were obtained in $CDCl_3$ using a 200 MHz Bruker instrument. A Perkin-Elmer LS-5 luminescence spectrophotometer was utilized for determining the fluorescence spectra of monomers and polymers, either in solution or on ITO electrodes (2–10 $\Omega\, cm^{-2}$, CNET Laboratory). The stock solutions [concentrations 10^{-3} M for monomers and 9.6×10^{-4}–3.3×10^{-4} mol of repeat unit (r.u.) l^{-1} for polymers] were diluted to obtain concentrations of 10^{-4}–10^{-5} M (monomers) and 6.6×10^{-5}–9.6×10^{-6} mol r.u. l^{-1} (polymers) for fluorescence measurements.

Molecular weights

Molecular weights were determined by gel permeation chromatography (g.p.c.) against polystyrene standards by using a Waters instrument and THF as eluting solvent (1 ml min^{-1}). Microstyragel columns with porosities of 10^5, 10^4, 10^3, 500 and 100 Å were used in series.

Conductivity measurements

Measurements were performed by either a two-probe technique using a Wayne Kerr conductimeter model Autobalance Universal Bridge B642, or a four-probe technique using a laboratory-constructed device. Samples were prepared as thin films (thickness $\approx 200\ \mu m$) or as pressed pellets obtained under a pressure of $5 \times 10^6\ kg\, cm^{-2}$ (thickness $\simeq 0.1$–0.2 mm).

RESULTS AND DISCUSSION

Electrochemistry

By applying an anodic polarization to the platinum electrode in a 0.1 M $TBABF_4$ acetonitrile solution of the monomer, we observed the formation of a polymer film at the surface of the electrode, with oxidation potentials at 1.1 V for **1**, 1.0 V for **2** and 1.2 V for **3**. These values are significantly lower than the reported 1.9 V for benzene[14], which is due to the mesomeric effect of alkoxy groups. The films formed at the electrode grew steadily during successive cyclic potential scans between 0.3 V and 1.8 V. In contrast to the electropolymerization of benzene or biphenyl[14], the oxidation potential values of the alkoxy monomers and of the corresponding polymers are very close. A very slight difference was found between the oxidation potential of the first cycle (corresponding to oxidation of the monomer), and those of the following cycles (*Figure 1*). During the back sweep, a large reduction peak was produced, its intensity increased regularly with the number of cycles, which can be related to the increase of thickness of this conducting film (*Figure 1*). This is a general behaviour of conducting electrosynthesized polymers.

The deposit formed after about eight cycles consisted of a brown, fibrillar, relatively thick film. Moreover, filaments appeared in the solution. After polarization at a potential of 1.8 V a doped material was obtained.

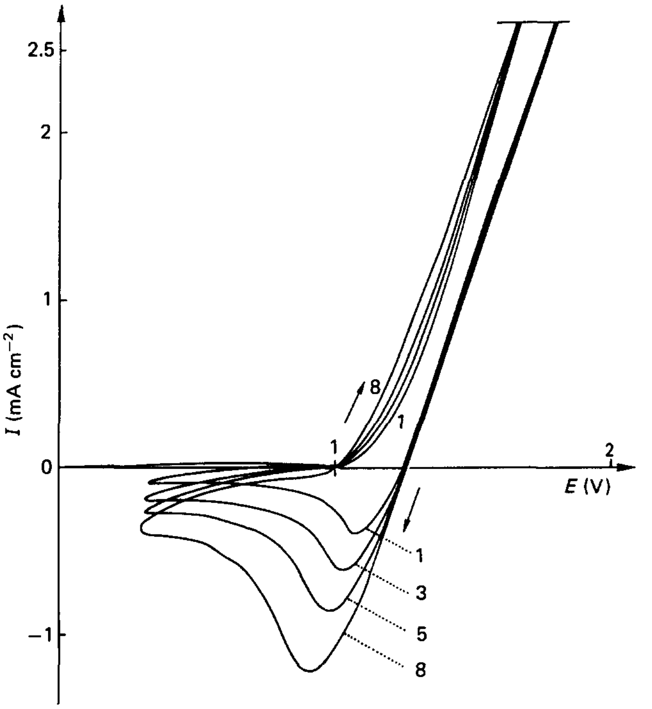


Figure 1 Cyclic voltammograms for 10^{-2} M 1-methoxy-4-n-hexoxybenzene (scan rate 100 mV s^{-1}) recorded in 0.1 M $TBABF_4$ acetonitrile solution with one, three, five and eight cycles

Polymer structure

Infra-red spectral analysis of the monomers and polymers provides important information on the structure of the materials. The main i.r. absorption bands for PMEP, PMHP, PMAP and their monomers, together with their assignments are given in *Table 1* (*Figures 2–4*). The aromatic C–H stretching vibrations in the 3010–3030 cm^{-1} region are much weaker for

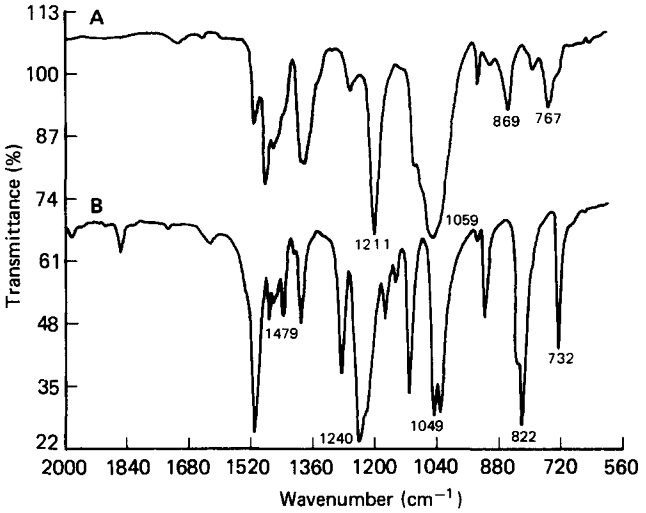


Figure 2 Fourier transform infra-red absorption spectra of (A) PMEP and (B) its monomer in KBr pellets

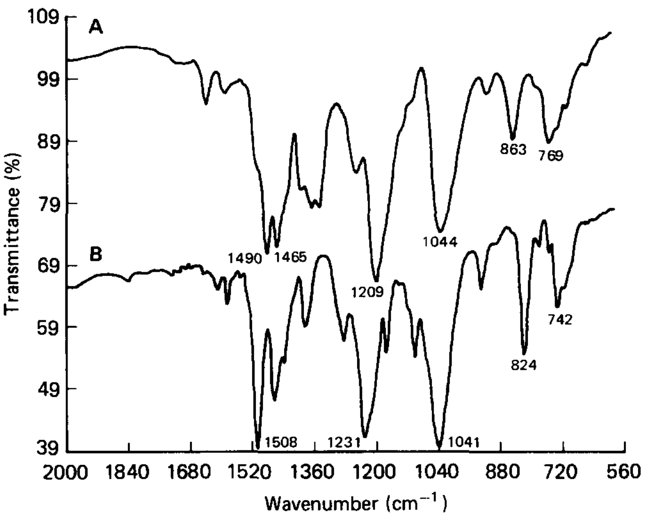


Figure 3 Fourier transform infra-red absorption spectra of (A) PMHP and (B) its monomer in KBr pellets

Table 1 Infra-red absorption band positions and assignments for monomers and polymers (cm^{-1})

Compound	Aromatic C–H	Aliphatic C–H	Aromatic ring stretching	Methyl deformation	Aromatic/aliphatic C–O–C		Aromatic C–H out-of-plane
					Asymmetric	Symmetric	
MEB	3072, 3048	2983, 2954, 2935	1512, 1479, 1441	1396	1240	1049	822, 732
PMEP	3030	2965, 2938, 2877	1492, 1475	1393	1211	1059	870, 767
MHB	3065, 3045	2933, 2860, 2834	1508,1467, 1442	1389	1232	1042	824, 742
PMHP	3050	2952, 2930, 2857	1491, 1465	1379	1209	1044	863, 769
MAB	3051, 3008	2912, 2890, 2850	1507, 1454, 1446	1374	1225	1077	821, 713
PMAP	–	2989, 2905, 2849	1484, 1453	1394	1207	1046	865, 769

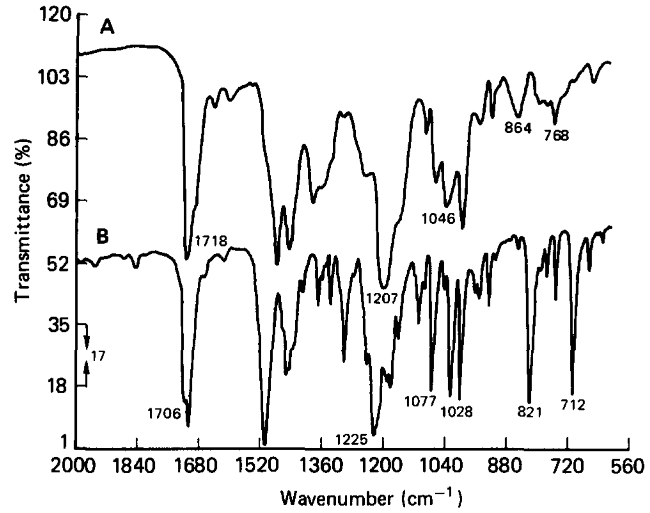


Figure 4 Fourier transform infra-red spectra of (A) PMAP and (B) its monomer in KBr pellets

PMEP and PMHP than for the corresponding monomers.

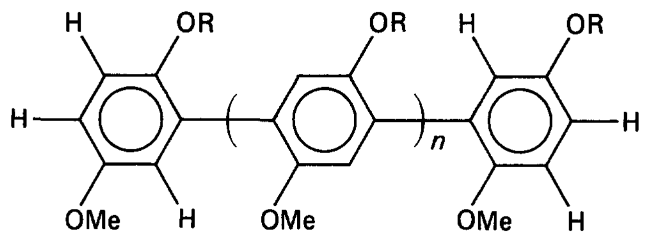
The carbonyl C=O stretching band which occurs at ~1706 cm^{-1} in MAB is shifted to ~1719 cm^{-1} in the corresponding polymer (*Figure 4*), which indicates the existence of significant steric interactions between the CH_2COAd (Ad = adamantyl) groups located on the polymer chain. The absorbances due to the aromatic ring vibrations are found in the vicinity of 1510–1440 cm^{-1} for all monomers and polymers; these bands are shifted towards shorter wavenumbers for the polymers.

The C–H out-of-plane vibrations located at ~820–825 and 715–740 cm^{-1} in the monomers are characteristic of 1,4-disubstituted benzenes. In the case of polymers these bands disappear, as expected; two new absorption bands appear at ~865–870 and 767–769 cm^{-1}. The first one is of medium intensity, and it is typical of a C–H out-of-plane vibration for 1,2,4,5-tetrasubstituted benzenes[15].

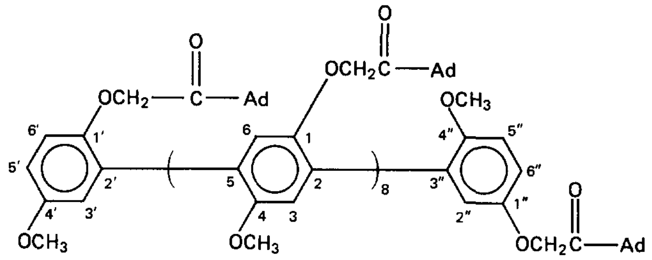
Therefore, it is characteristic of a chain coupling *para* for the three polymers. Moreover, another band, of weaker intensity, occurs at ~805 cm^{-1}, indicating the presence of 1,2,4,5-tetrasubstituted phenylene groups[15]. In contrast, no band is observed in the 840–850 cm^{-1} region which is specific to a chain coupling meta (1,2,3,5-tetrasubstituted phenylene groups). Consequently, the structure in *Scheme 4* can be proposed for these polymers.

The band at ~767–769 cm^{-1} is of medium intensity, and can be attributed to a C–H out-of-plane vibration of the terminal hydrogens in the 1,2,5-trisubstituted aromatic rings[15].

Our structural characterization (*Scheme 4*) is in good agreement with that established by Yamamoto *et al.*[9] and Le Berre *et al.*[10] for poly(2,5-dimethoxy-1,4-phenylene). Also, for comparison purposes, we constructed molecular models of fragments of poly(2-methoxy-5-alkoxy paraphenylene) and poly(2-methoxy-5-alkoxy metaphenylene). We found that very severe steric crowding between alkoxy substituents (such as hexoxy and adamantyloxoethoxy groups) prevents chain coupling *meta*, while steric effects are much less important for chain coupling *para*. These molecular model results support our structural identification.



Scheme 4



Scheme 5

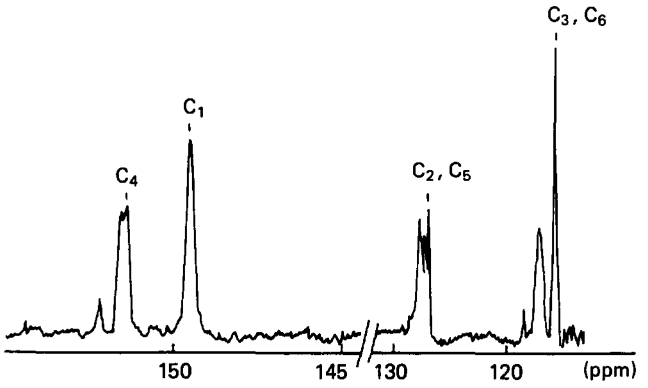


Figure 5 Aromatic region of the ^{13}C n.m.r. spectrum of PMAP in $CDCl_3$ solution. The main signals (due to aromatic carbons of the phenylene repeat units) are assigned

In order to confirm the structure of polymers, we also investigated the ^{13}C n.m.r. spectra. The n.m.r. spectrum of MAB is characterized by ^{13}C signals at 151.96 (C_1), 153.48 (C_4), 115.35 (C_3, C_5), and 114.42 ppm (C_2, C_6) (*Scheme 1*). In the case of PMAP, the main ^{13}C aromatic signals of the polymer chain occur at 149.49 (C_1), 151.52 (C_4), 127.01 (C_2, C_5), 115.65 (C_3, C_6) (*Scheme 5* and *Figure 5*). The 127.01 ppm value for C_2 and C_5 indicates that a *para* coupling of the chain is formed at these aromatic sites. This finding is similar to the observation of Yamamoto *et al.*[9] in the case of the ^{13}C n.m.r. spectrum of poly(2,5-dimethoxy-1,4-phenylenes). These authors found also that *para* coupling occurred in their compound, although steric crowding is much less severe than in our case. We observed also less intense ^{13}C signals at 151.2 ($C_{1'}$), 152.2 ($C_{4'}$), 127.2 ($C_{3''}$), 127.7 ($C_{2'}$), 118.4 ($C_{2''}$, $C_{3'}$) and 117.0 ($C_{5'}$, $C_{6'}$, $C_{5''}$, $C_{6''}$), which are characteristic of the aromatic carbons of termination phenylene groups (*Figure 5*).

We found similar ^{13}C n.m.r. spectral features for PMHP.

X-ray analysis of PMEP, PMHP and PMAP shows that these polymers are amorphous.

Polymer physical properties

We found that PMEP is only very weakly soluble in several organic solvents such as methylene chloride, chloroform and THF. In contrast, the neutral states of PMHP are soluble ($\simeq 1$ mg ml^{-1}), and those of PMAP are very soluble ($\geqslant 5$ mg ml^{-1}) in usual organic solvents, including methylene chloride, chloroform, carbon tetrachloride, THF and dimethylformamide.

This demonstrates that the introduction of a relatively long, flexible alkyl chain in the alkoxy group significantly enhances the solubility of these polymers. Moreover, the substitution of a –CO– adamantyl side chain into the methoxy group also dramatically increases their solubility probably due to the lipophilic properties of the adamantyl substituent.

The molecular weight of PMEP could not be determined by g.p.c. because of the poor solubility of this polymer. For PMHP and PMAP the number average molecular weights measured by g.p.c. are, respectively, 2200 ($M_w = 3300$) and 2900 ($M_w = 4100$). These data give average *DP* values of ~11 for PMHP and ~10 for PMAP with relatively small polydispersities (values between 1.4 and 1.5). These *DP* values should only be taken as approximate, since the comparison of polystyrene standards with conjugated polymers does not provide exact results.

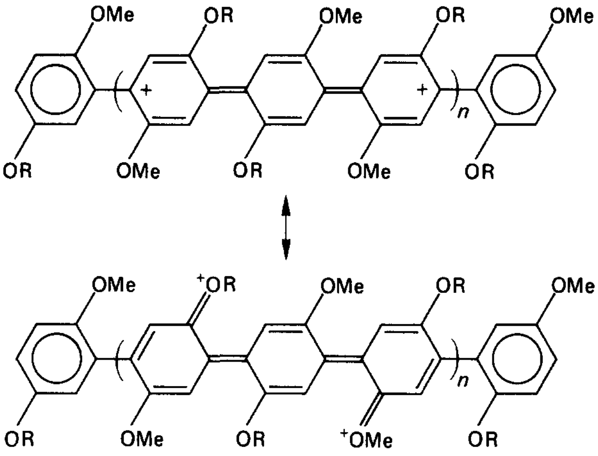
Although *DP* values of ~10–11 are relatively low it must be stressed that soluble, functionalized polyparaphenylenes (PPP) with *DP* of this size constitute the longest electrosynthesized polymers of this kind known presently. Chemically synthesized, soluble poly(*p*-2,5-di-n-alkylphenylene)s have been recently described[11], with an average *DP* of the order of 13–28.

Polymer electrical conductivities

In their neutral form, PMEP, PMHP and PMAP are insulating polymers. In contrast, when they are doped electrochemically using $TBABF_4$ or $LiAsF_6$ as electrolytes, they become semiconductive powders, as shown by the conductivities reported in *Table 2*. The conductivity values of oxidized polymers range between 2×10^{-5} S cm^{-1} and 2×10^{-2} S cm^{-1}. These values are much lower than those generally observed[16] for the conductivities of unsubstituted, doped PPP, which are of the order of 500 S cm^{-1}. The difference in the dopant level as well as the nature of the charge carrier can explain these large variations in conductivities.

In the case of the poly(2,5-dialkoxy paraphenylene)s, two possible effects might contribute to a decrease of the conductivity of these substituted polymers relative to PPP. First, two possible resonance forms IA and IB can be postulated for the commonly accepted bipolaronic charge carrier (*Scheme 6*).

Therefore, a significant part of the positive charge may be centred on one of the alkoxy side chains (form IB). This charge is more localized than in structure IA, and it could explain the decrease of carrier mobilities and of conductivities of these substituted polymers relative to PPP. Second, the presence of large substituents on the main polymer backbone could also produce a distortion in the chain resulting in the decrease of the migration of the charges.



(IA)

(IB)

Scheme 6

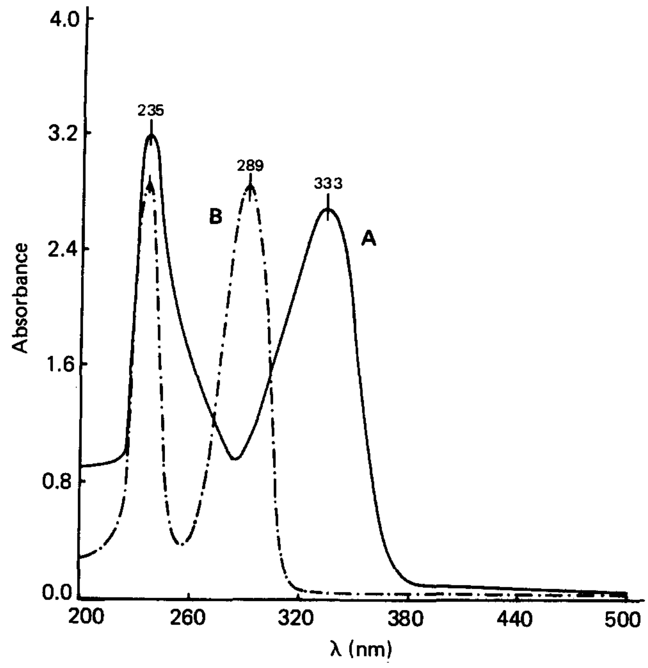


Figure 6 Ultraviolet absorption spectra of (A) 3.3×10^{-4} r.u. l^{-1} PMAP and (B) 10^{-4} M MAB in dichloromethane solution

Table 2 Electrical conductivities for oxidized polymers (S cm^{-1})

Polymer[a]	$TBABF_4$[b]	$LiAsF_6$[b]
PMEP	2×10^{-2}	–
PMHP	$2\text{–}7 \times 10^{-5}$[c]	–
PMAP	–	1×10^{-4}[c]

[a] Conductivities were measured on polymer films unless otherwise stated
[b] Electrolyte concentration 10^{-1} M
[c] Conductivity measurements were also performed on pellets

Ultraviolet absorption spectroscopic studies

The u.v. absorption spectra were obtained for the monomers and for the polymers in solution (*Figure 6*), and also for the polymers as thin films chemically deposited on ITO glass (*Table 3*). The spectral characteristics of monomers are practically identical, with two maxima at ~220–235 (^1L_a band) and 290 nm (^1L_b band), corresponding to the π–π^* transition. As expected from the strong electron-donating properties of the two alkoxy groups in the *para* position, the ^1L_a and ^1L_b bands of these compounds are significantly red-shifted relative to those of monoalkoxybenzenes.

The absorption spectra of the corresponding polymers in solution also exhibit two maxima; in the case of PMEB and PMHB, important red shifts (between 16 nm and

Table 3 Ultraviolet absorption spectral characteristics of monomers and polymers

	Solution		Film[d]
Compound[a]	Solvent	λ_A (nm)[b,c]	λ_A (nm)[c]
MEB	EtOH	220 (4.48), 290 (4.32)	–
PMEB	CH_2Cl_2	236 (3.97), 330 (3.87)	323
MHB	THF	237 (4.00), 291 (4.25)	–
PMHB[e]	THF	259 (3.17), 330 (3.46)	307
MAB	CH_2Cl_2	235 (4.46), 289 (4.45)	–
PMAB	CH_2Cl_2	235 (3.99), 333 (3.91)	334

[a] Concentration was 10^{-4} M for monomers and 3.3×10^{-4} mol r.u. l^{-1} for polymers unless otherwise stated

[b] Log ε_{max} [in $l\,cm^{-1}\,(mol)^{-1}$ for monomers and in $l\,cm^{-1}\,(r.u.)^{-1}$ for polymers] in parentheses

[c] Precision of wavelength is ±1 nm

[d] Film deposited on an ITO plate after evaporation of the polymer chloroformic solution

[e] PMHB concentration 9.6×10^{-4} mol r.u. l^{-1}

40 nm) of both bands are observed relative to the monomers. In contrast, only the ^1L_b band of PMAB shows a 44 nm red shift relative to that of MAB (*Figure 6*). These shifts imply a more extensive electronic delocalization in the polymeric chains. However, the absorption peaks of PMEP, PMHP and PMAP are located at ~3.7 eV, while PPP films present absorption maxima between 3.6 eV and 3.2 eV, depending on the method of preparation[14,16,17]. One would expect a lowering of the π–π^* transition energy in the case of poly(dialkoxyparaphenylene) relative to that of PPP due to the presence of dialkoxy groups, while the reverse behaviour is seen. This surprising result clearly indicates that the conjugation of the chains of these new polymers is unexpectedly poor. It could be due to the steric requirements of the bulky alkoxy groups which would force them to lie above and below the plane of the polymer chains. It might result also from the presence of chain segments of shorter effective conjugation length in the relatively short-chain PMHP and PMAP, as compared to the long-chain PPP.

Also, the polymers show significant hypochromism with respect to the monomers, as indicated by the comparison of log ε_{max} (*Table 3*). This diminution of absorption intensity is due to the interactions between ground and singlet excited electronic states of neighbouring chromophores, and depends on their geometric configuration. It indicates a stacked arrangement of dialkoxybenzene chromophores in the polymer chains. A similar conclusion was reached recently in the case of the u.v. spectral properties of polymers containing pyrene and carbazole groups[18].

The absorption spectra of solid films of PMEB and PMHB (*Figure 7*) show a slight hypsochromic (blue) shift compared to solution, while no significant wavelength change between the two phases is observed for PMAB. These moderate shifts indicate that the conformational changes of these polymers are not very important upon dissolution. These results are in contrast with recent u.v. spectral data which showed that the conformation of soluble poly(3-alkylthienylenes)[3] and ethylmercapto-substituted polythiophenes[8] was more disordered in solution than in the solid state. This difference of behaviour may be due to the fact that poly(2,5-dialkoxyparaphenylenes) present a more planar, rigid structure, which would be less deformable in solution than that of substituted polythiophenes. Also, the half-bandwidths are significantly wider in the solid film than in solution for all poly(2,5-dialkoxyparaphenylenes) under study, indicating more important interchain associations in the solid state. It is also worthwhile to note that the band gap (onset of the π–π^* transition) of PMEB, PMHB and PMAB is at ~3.30, 3.25 and 3.15 eV, which is slightly higher than that of PPP films (3.02 eV)[14]. This higher band gap could be due to the presence of the two bulky alkoxy substituents provoking a slightly distorted, preferred conformation. A similar interpretation was postulated recently in the case of soluble ethylmercapto-substituted polythiophenes, for which a 10° increase of the twist angle was found to result in an increase of ~0.2 eV of the band gap[8].

Fluorescence spectral studies

The room-temperature excitation and emission fluorescence spectral characteristics of monomers and polymers in solution, and of polymers in solid films are reported in *Table 4*.

The fluorescence excitation spectra of monomers are characterized by one maximum at ~290 nm, while a second, less intense peak occurs at 242 nm in the case of MAB. In contrast, the excitation spectra of polymers in solution present two maxima at ~236–245 and 330–340 nm (*Figures 8* and *9*). The latter peak is significantly more intense than the former peak. These wavelength values are very close to those determined for absorption spectra, for the monomers as well as for the polymers. In the solid state, the excitation spectra of PMEB and PMHB exhibit a maximum at ~330 nm, a value which is almost identical to that obtained in solution. In the case of PMAB film, the fluorescence excitation maximum undergoes a 20 nm red shift, relative to the corresponding peak determined in solution (*Figure 10*). Also, the excitation band of PMAB is much wider in the solid state than in solution. These features confirm the existence of significant interchain interactions of

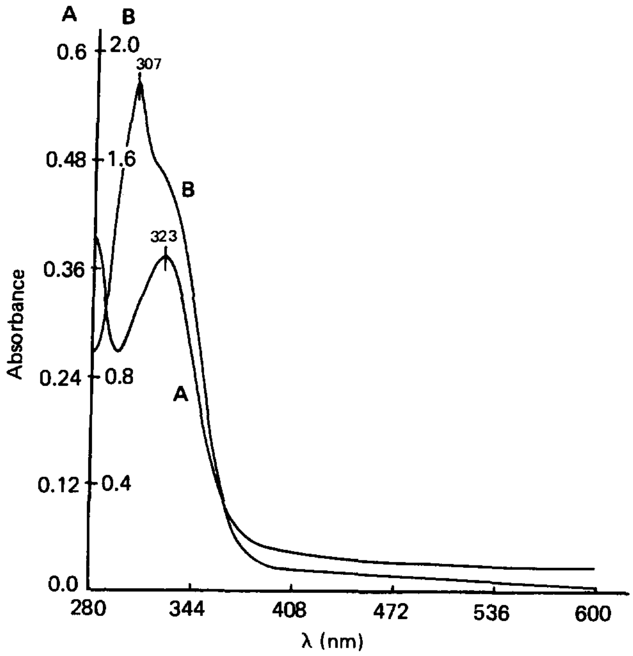


Figure 7 Solid-state u.v. absorption spectra of (A) PMEB and (B) PMHP films deposited on ITO plate

Table 4 Excitation and emission fluorescence characteristics of monomers and polymers

	Solution			Film[d]	
Compound[a]	Solvent	λ_{ex}[b,c] (nm)	λ_{em}[c] (nm)	λ_{ex}[c] (nm)	λ_{em}[c] (nm)
MEB	EtOH	287	325	–	–
MEB	CH_2Cl_2	290	328	–	–
PMEB	CH_2Cl_2	243 (93), 333 (100)	398	329	396
MHB	THF	292	326	–	–
PMHB[e]	THF	236 (70), 331 (100)	398	330	390
MAB[f]	CH_2Cl_2	242 (31), 290 (100)	327	–	–
PMAB[g]	CH_2Cl_2	244(88), 339 (100)	402	360	406

[a] Concentration was 10^{-5} M for monomers and 6.6×10^{-5} mol r.u. l^{-1} for polymers unless otherwise stated
[b] Relative intensities in parentheses
[c] Precision of wavelength is ± 1 nm
[d] Film deposited on an ITO plate after evaporation of the polymer chloroformic solution
[e] Concentration 9.6×10^{-6} mol r.u. l^{-1}
[f] Concentration 10^{-4} M
[g] Concentration 3.3×10^{-5} mol r.u. l^{-1}

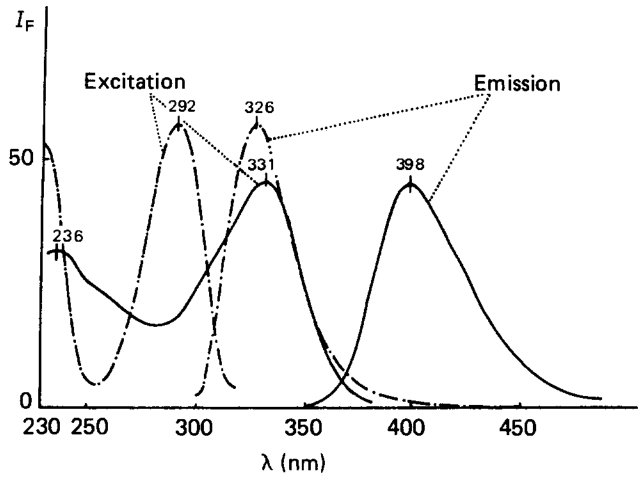


Figure 8 Excitation and emission fluorescence spectra of 10^{-5} M MHB (–·–·–) and 9.6×10^{-6} mol r.u. l^{-1} PMHP (———) in THF solution

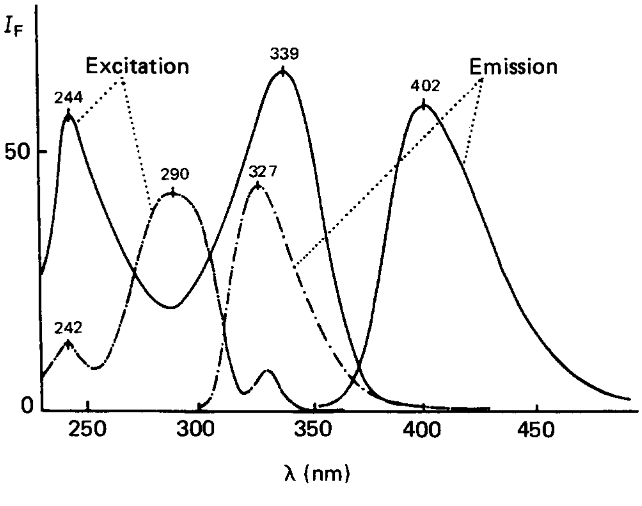


Figure 9 Excitation and emission fluorescence spectra of 10^{-4} M MAB (–·–·–) and 3.3×10^{-5} mol r.u. l^{-1} PMAP (———) in dichloromethane solution

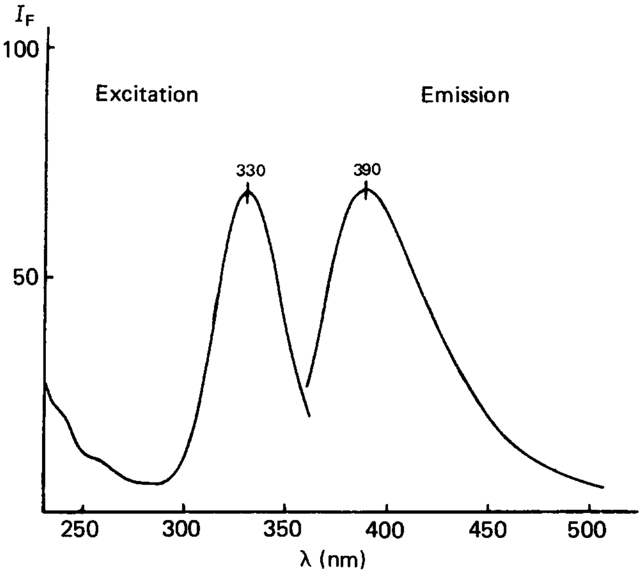


Figure 10 Solid-state excitation and emission fluorescence spectra of PMHP film deposited on ITO plate

PMAB and of a variety of configurations in the film, due to the steric effect of the bulky adamantyl substituents, and/or to the dipole/dipole interactions of the carbonyl groups.

The fluorescence emission spectra recorded in solution exhibit only one broad structureless maximum (half-width ~0.4 eV) occurring at ~326 nm (3.80 eV) for the monomers and at ~400 nm (3.10 eV) for the polymers (*Figures 8* and *9*). The emission wavelength maxima of polymer films are very close to those obtained in solution (*Table 4* and *Figure 10*). The absence of any vibronic structure in the fluorescence emission of polymer films and solutions can be attributed to inhomogeneous broadening of the bands originating from the disordered conformation of the polymer chains. It is in marked contrast with the structured, low-temperature emission fluorescence spectra of better ordered polymers, such as poly(*p*-phenylenevinylene)[19] and poly(phenyl phenylenevinylene)[20]. There is no significant difference between the position of the emission band of PMEB, PMHB and PMAB, showing that the energy level of the excited singlet states of polymers is not affected by the variation of the chemical nature of the alkoxy side chain. The dramatic red-shift ($\sim$0.70 eV) of the emission maximum of the polymers relative to the molecular emission of the monomers can be attributed to two causes. First, the extension of the π-electron delocalization throughout the polyaromatic chain may be enhanced by the mesomeric electron-donating effect of the alkoxy group. This increases the double-bond character of the carbon–carbon bond between phenylene groups. Second, the formation of excimers may occur between aromatic groups of the polymer chains, resulting generally in the appearance of a red-shifted, broad and structureless emission band[21]. More information concerning the fluorescence lifetimes of monomers and polymers would be needed to confirm the formation of poly(dialkoxy-paraphenylene) excimers.

The Stokes shift, measured between the absorption and fluorescence peaks of PMEB, PMHB and PMAB, is close to 0.65 eV. In terms of the Bredas theory[22,23] it corresponds to the location of two exciton–polaron levels at $\sim$0.32 eV from the valence and conduction bands, respectively. Our Stokes shift values are close to those found recently for the absorption and fluorescence spectra of poly(3-alkylthienylene) solutions[3] and of polyparaphenylene films[14] and matrix-isolated poly(4,4′-diphenylenediphenylvinylene)[20]. Such relatively large Stokes shifts found in the case of polymers have been recently attributed to the presence of chain segments of various effective conjugation length[20].

CONCLUSIONS

Electrosynthesized poly(2-methoxy-5-hexoxypara-phenylene) and poly{[2-(1-adamantyl)-2-oxoethoxy]-paraphenylene} constitute both soluble and conjugated polymers in the reduced state. These new materials can be electrochemically cast into relatively thick films, although the *DP* is relatively low. The doped conductivities of PMHP and PMAP range between 2×10^{-5} S cm^{-1} and 10^{-4} S cm^{-1}. Our *FT*i.r. and n.m.r. results show the formation of regular polymeric chains with *para* coupling. The absorption and fluorescence spectra demonstrate that the conjugated electronic structure of these polymers does not change significantly after dissolution and processing into solid thin films. The band gap values and the absence of vibronic structure indicate the existence of distorted, disordered conformations of the polymer chain resulting mainly from the effect of the bulky alkoxy substituents. The important red shift of the polymers fluorescence maximum relative to the corresponding monomers is consistent with the delocalization of the π-electron system and with the possible formation of excimers. More generally, the concept of exciton–polaron states postulated recently in the study of the solid-state conducting, unsubstituted polyparaphenylenes[14] can be extended to analogous functionalized polymers in solution.

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