Organic conducting polymers: synthesis, characterization and conductivity of polyethynylfluorenol

M. V. Russo*, G. Iucci, G. Polzonetti and A. Furlani
Department of Chemistry, University 'La Sapienza', P.le A. Moro 5, 00185 Rome, Italy

(Received 17 April 1991; revised 26 July 1991; accepted 27 November 1991)

The polymerization reactions of ethynylfluorenol (EFl) in the presence of Rh(I), Pt(II), Pd(II) and WCl_6 catalysts have been investigated. The polymer (PEFl) is air stable and soluble; in solution PEFl slowly releases some of the pendent groups which are converted into 9-fluorenone. Upon doping, enhancement of the conductivity up to about 10 orders of magnitude can be achieved. X.p.s. measurements performed on I_2-doped PEFl suggest that I_5^- is the major doping species. An interesting reversible response to relative humidity variations is found for $FeCl_3$-doped samples.

(**Keywords: polyethynylfluorenol; conductivity; X.p.s.**)

INTRODUCTION

Organic conducting polymers[1,2] have been the object of extensive studies owing to their electrical properties, which render them promising materials for electronic devices. Among the polyconjugated systems so far investigated, polyacetylene (PA) is the most widely studied both from a theoretical point of view[3,4] and in the context of electronic applications[4].

Poly(substituted)acetylenes $(-CH{=}CR-)_n$, where R = alkyl or phenyl group, normally show lower conductivity upon doping[5–8] in comparison with PA. However, air stability, solubility, processability[9,10], optical properties[11], and feasibility in the realization of electronic devices of these materials give an outstanding input to the synthesis and the study of new poly(substituted) acetylenes.

In the last decade we have prepared a variety of $(-CH{=}CR-)_n$ polymers[6,12–15]. We have investigated polyphenylacetylene (PPA) more extensively, studying the conductivity of samples with different percentages of *cis* content, doped either homogeneously with various doping agents[6,15–17], or heterogeneously by exposure of films to I_2 vapours[18]. In the use of PPA no direct correlation between *cis*/*trans* configuration or stereoregularity of the PPA chain and conductivity could be shown[15].

In this paper we report a study of the polymerization reactions of ethynylfluorenol (EFl), an alkyne carrying a bulky substituent which should lead to a linear chain with repeat units $-[CH{=}C(C_{13}H_9O)]_n$, as reported in *Figure 1*. This monomer was chosen in order to investigate the influence of a bulky pendent group in the polymer chain, on the properties of the final reaction products, in comparison with the properties of known poly(substituted) acetylenes, in particular PPA. The characterization of undoped and doped polyethynylfluorenol (PEFl) carried out by i.r., optical absorption, X.p.s. and n.m.r. spectroscopies together with the electrical properties of doped samples will be reported and discussed.

EXPERIMENTAL

Methods and instrumentation

I.r. spectra were run on a Perkin-Elmer model 580 B spectrometer as nujol mulls or films obtained by evaporating CH_2Cl_2 solutions of the polymer on NaCl optical cells. U.v. spectra were run on a Perkin-Elmer Lambda 5 spectrometer.

^1H and ^{13}C n.m.r. spectra were recorded on a Varian X-L300 spectrometer in $CDCl_3$. Molecular weights (M_w) were measured by a Knauer Osmometer model 11 at 30° using $CHCl_3$ as the solvent. Softening temperatures were measured with a Kofler apparatus. Elemental analyses were carried out at the Università di Pisa, Italy. Conductivity measurements were performed on pressed pellets (thickness ~ 0.1 cm, diameter ~ 1.3 cm) prepared with a Specac hydraulic press P/N 150 at 8 tons, by using a Keithley 616 digital electrometer or a Keithley 580 Micro ohmmeter, as previously described[13].

X.p.s. was performed on a VG ESCA 3 MK1 instrument using $AlK\alpha_{1,2}$ radiation ($h\nu = 1486.6$ eV).

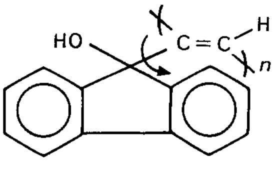

Figure 1 Proposed chemical structure of PEFl

---

*To whom correspondence should be addressed

0032-3861/92/204401-09

The typical vacuum in the analysis chamber was 1.33×10^{-7} Pa. PEFl films were cast from a CH_2Cl_2 solution onto a polished stainless steel probe.

Materials

9-Ethynyl 9-fluorenol (K&K), $[Rh(COD)Cl]_2$ (Stream Chemicals) and WCl_6 (Fluka AG, Chem.) commercial products were used without any further purification. All the solvents were reagent grade (Carlo Erba).

The complex [Rh(COD)im], (COD = *cis,cis*,cyclooctadiene, im = imidazole) was prepared from the reaction of $[Rh(COD)Cl]_2$ with imidazole; its structure, which is not completely known yet[19], is currently under investigation. $[Pd(PPh_3)_2Cl_2]$ and $[Pt(PPh_3)_2Cl_2]$ were prepared by the published methods[20].

$[Ni(C{\equiv}C{-}C_{13}H_9O)(NCS)(PPh_3)_2]$ ($C{\equiv}C{-}C_{13}H_9O$, EFl), $[Pt(EFl)_2(PPh_3)_2]$ and $[Pd(EFl)_2(PPh_2)_2]$ are new products.

Synthesis of $[Ni(NCS)(EFl)(PPh_3)_2]$. The complex was prepared according to the procedure previously reported[21] using $HC{\equiv}C{-}C_{13}H_9O$ as the acetylenic ligand.

Elemental analyses (%): calculated: C 73.78; H 4.61; found: C 73.30; H 4.57. M.p. 130–132°C with decomposition. U.v. ($CHCl_3$): λ_{max} 328, 275 nm (308 nm shoulder). I.r. selected bands (cm^{-1}): 3560 (w); 2100 (s); 1605, 1580, 1570 (w); 1480 (m); 1430 (s); 1180, 1160 (m); 1095 (s); 1080 (m); 980 (m); 850 (m); 770 (s), 745, 735 (s); 520, 510 (s).

Synthesis of $[Pd(EFl)_2(PPh_3)_2]$ *and* $[Pt(EFl)_2(PPh_3)_2]$. In a typical synthetic procedure, 200 mg of $[Pt(PPh_3)_2Cl_2]$ or 175 mg of $[Pd(PPh_3)_2Cl_2]$ ($\approx$0.25 mmol) were dissolved in diethylamine and 125 mg ($\approx$0.6 mmol) of EFl and 10 mg (0.05 mmol) of CuI were added. The reaction mixture was refluxed under stirring for 15 min, until a white solid precipitated. The solid was filtered off, washed with EtOH and recrystallized from $CHCl_3$/EtOH.

$[Pd(EFl)_2(PPh_3)_2]$. Elemental analyses (%): calculated: C 76.14; H 4.48; found: C 75.59; H 4.65. The compound decomposes before melting at 169–170°C. U.v. ($CHCl_3$) $\lambda_{max} = 280$ nm (310, 250 nm, shoulders).

$[Pt(EFl)_2(PPh_3)_2]$. Elemental analyses (%): calculated: C 70.14; H 4.29; found: C 69.83; H 4.27. M.p. 223–225°C. U.v. ($CHCl_3$) $\lambda_{max} = 312$ nm (322, 300, 250 nm shoulders). The Pt and Pd complexes show very similar i.r. spectra: 3570 (s), 2090 (m), 1320 (m), 1110, 1100, 1090 (m), 1060 (m), 980 (s), 770, 750, 730, 710, 695 (m-s), 520, 510, 500 (s) (cm^{-1}).

Polymerization reactions

The reactions were carried out under the following conditions.

Reaction with $[Rh(COD)Cl]_2$. EFl (1 g; 5 mmol) and 90 mg (0.125 mmol) of $[Rh(COD)Cl]_2$ (catalyst/monomer ratio = 1:40) were dissolved in 10 ml of C_6H_6; 1 ml of 0.2 M solution of NaOH in MeOH was added; the colour of the reaction mixture changed from light yellow to dark brown immediately.

Table 1 Polymerization reactions of EFl (reaction solvent C_6H_6)

Catalyst	Catalyst: monomer ratio	Reaction time (h)	Yield (%)	Softening point (°C)
$[Rh(COD)Cl]_2$/NaOH	1:40	20	90	144–153[a] 170–174[b]
[Rh(COD)Im]	1:50	20	–	
$[Pd(PPh_3)_2Cl_2]$	1:100	40	40	98–100
$[Pd(EFl)_2(PPh_3)_2]$	1:100	10	97	120–130[a] 154–160[b]
$[Pt(PPh_3)_2Cl_2]$	1:100	40	10	105–121
$[Pt(EFl)_2(PPh_3)_2]$	1:100	100	75	90–100
$[Ni(NCS)(EFl)(PPh_3)_2]$	1:100	35	–	
WCl_6	1:50	12	12	

[a] Crude PEFl

[b] PEFl crystallized from THF/petroleum ether

Reactions with WCl_6 *and* [*Rh*(*COD*)*Im*]. EFl (1 g; 5 mmol) and ~50 mg of the catalyst were dissolved in 10 ml of C_6H_6.

Reactions with Pt, Pd and Ni catalysts. EFl (1 g; 5 mmol) and 0.05 mmol of the catalyst (catalyst/monomer ratio $\approx$ 1:100) were dissolved in 10 ml of C_6H_6.

In all cases the reaction mixtures were refluxed for 10–100 h (see *Table 1*), then concentrated under reduced pressure. After addition of petroleum ether at 30–50°C, PEFl precipitated as a brown powder, which was filtered off and dried under vacuum. PEFl is soluble in many organic solvents such as C_6H_6, $CHCl_3$, CH_2Cl_2, CH_3COCH_3, CH_3OH, C_2H_5OH and can be recrystallized from benzene/petroleum ether.

Doping procedures

Doping with I_2, $FeCl_3$, $NaBH_4$, $SnCl_2$. Weighed amounts of PEFl and of the various dopants were dissolved in tetrahydrofuran (THF). Every solution was aged for 24 h, then the solvent was removed under reduced pressure.

Doping with HCl or H_2SO_4. PEFl (250 mg) was dissolved in acetone and 2 ml of a mixture of acid: H_2O (ratio 1:1) (HCl, $d = 1.186$ g ml^{-1}, nominal doping 63% w/w; H_2SO_4 $d = 1.835$ g ml^{-1}, nominal doping 85% w/w) was added to the solution. After 24 h the acetone was removed under reduced pressure and water was added in order to precipitate the doped polymer, which was filtered and dried over $CaCl_2$.

Doping with $HClO_4$. PEFl (250 mg) was dissolved in THF and 0.6 ml of a mixture of $HClO_4$: H_2O (ratio 1:1) ($HClO_4$ $d = 1.53$ g ml^{-1}, nominal doping 50% w/w) was added. After 24 h, THF was removed under reduced pressure; the doped polymer was precipitated with water filtered off and dried over $CaCl_2$. Samples of the doped polymer were pressed into pellets for the d.c. conductivity measurements.

Investigations on the stability of PEFl

PEFl (500 mg) was dissolved in about 200 ml of different solvents ($CHCl_3$, C_6H_6, THF) and aged at room temperature for about 30 days or refluxed for about 5 days. The solvent was then evaporated. Solid products were recovered and then chromatographed on a SiO_2 column, using $CHCl_3$ as eluent.

Oxidation of PEFl

A solution of 200 mg of PEFl in 20 ml of $CHCl_3$ was stirred with aqueous $KMnO_4$ (≈ 2 N) for about 1 h; then the reaction mixture was filtered and the aqueous phase was discarded. The chloroform phase was dried over $CaCl_2$ and the solvent evaporated. Oxidized PEFl was chromatographed on a SiO_2 column using chloroform as eluent.

Oxidation of EFl

A chloroform solution of EFl was refluxed under stirring for about 10 h with aqueous $KMnO_4$. The reaction mixture was filtered off, the chloroform phase was separated from the aqueous phase and dried over $CaCl_2$; the solvent was evaporated. Oxidized EFl was chromatographed in a SiO_2 column using $CHCl_3$ or C_6H_6 as eluents.

The eluted fractions recovered from the chromatographic separations were further examined by thin layer chromatography (t.l.c.) and characterized by i.r. and n.m.r. spectroscopies.

RESULTS

Polymerization reactions of EFl

Data concerning the polymerization reactions are collected in *Table 1*. $[Rh(COD)Cl]_2$ and $[Rh(COD)im]$ complexes have been used because they were found to be very active catalysts in the polymerization of phenylacetylene (PA), giving a stereoregular polymer[22] and free-standing films[19]. Here only the $[Rh(COD)Cl]_2$ complex was found to be active towards EFl giving PEFl in high yield ($\sim 90\%$).

The Pt, Pd and Ni complexes with the alkyne ligand σ-bonded to the metal ion are new products synthesized for this work. Previous investigations on the polymerization of mono(substituted)acetylenes showed that the presence of a metal-carbon σ-bond in the catalyst can enhance the reaction rate giving good polymer yields[23,24]. $[Pt(PPh_3)_2Cl_2]$ and $[Pd(PPh_3)_2Cl_2]$ have been used as catalysts for comparison with the corresponding acetylides. $[Ni(NCS)(EFl)(PPh_3)_2]$ was also tried but was found to be completely ineffective. Among these complexes the best yields were obtained by using $[Pd(EFl)_2(PPh_3)_2]$ and $[Pt(EFl)_2(PPh_3)_2]$, the latter being less active.

WCl_6 has been tested as it was reported to be an effective catalyst for the polymerization of PA giving PPA of high molecular weight[25], but no good results have been obtained with EFl.

The molecular weights (osmometric) of PEFl obtained with the catalysts fall in the range from 600 (Pt, Pd catalysts) to 1000 (Rh-W catalysts) amu. The M_w of crude PEFl is low; oligomers rather than high polymers of EFl are obtained. Fractions with M_w up to 2000 amu, corresponding to about 10 monomer units, are separated when the crude polymer is chromatographed on a SiO_2 column. It is worth noting that the osmometric measurements, which are based on vapour pressure variations of solvent and polymer solution, underestimate the M_w because the presence in solution of low oligomer fractions cannot be excluded. Therefore polymer chains with more than 10 monomer units are reasonably obtained.

The elemental analyses of crude PEFl are in good agreement with the theoretical values: for example PEFl obtained with $[Pd(EFl)_2(PPh_3)_2]$: found (%) C 86.88; H 5.72, calculated for $C_{15}H_{10}O$: C 87.36; H 4.89. Recrystallization from benzene/petroleum ether, however, gives products with lower carbon and hydrogen content, indicating a partial modification of the initial products.

Characterization of PEFl

I.r. spectra. The i.r. spectra of the monomer and of the polymer (PEFl) are reported in *Figure 2*A and **B**. In the range 700–800 cm^{-1} the monomer gives three sharp strong bands at 770, 755 and 730 cm^{-1}, which can be assigned to the out-of-plane deformation vibration of the hydrogen atoms attached to the benzene ring when it is *ortho*-disubstituted with cyclic structures[26]. This pattern, less well resolved, is also found in the spectrum of the polymer (*Figure 2B*). The bands at 900, 1000, 1060, 1200 and 1280 cm^{-1} present in the spectrum of the monomer are usually attributed to in-plane C–H deformation vibrations of the aromatic compounds. These bands appear shifted and of lower intensity in the spectrum of PEFl.

The polymer spectrum shows a broadening of bands in the O–H stretching mode region with maxima at ~ 3540 and 3350 cm^{-1}, which indicate that the –OH groups are situated in different chemical environments and involved in intra- and/or interchain hydrogen bonding. The band at 2100 (w) cm^{-1}, albeit weak in the monomer, is absent in the polymer. The disappearance of this band is a common feature in the monosubstituted acetylene polymers' spectra and indicates that the chain growth proceeds through the opening of the triple bonds. The two bands at 1600 and 1580 cm^{-1} (C=C stretching mode of the aromatic system) are retained in the spectrum of PEFl. The structure of the pendent group seems to remain unchanged upon the polymerization reaction. The i.r. spectra of PEFl synthesized with different catalysts are quite similar to that reported in *Figure 2B*.

U.v. spectra. The optical absorption spectra ($CHCl_3$ solutions) of EFl and PEFl are reported in *Figure 3A* and *B*, respectively. The monomer shows a maximum at $\lambda = 277.0$ nm ($\varepsilon = 1.20 \times 10^4$) and a shoulder at $\lambda = 285$ nm; the polymer gives a maximum at $\lambda = 269.0$ ($\varepsilon = 1.21 \times 10^4$, calculated on monomer unit) and a broad absorption at $\lambda \approx 400$ nm (3.10 eV).

^1H and ^{13}C n.m.r. spectra. The ^1H n.m.r. spectra of EFl and PEFl are reported in *Figure 4a* and *b*. In the range 7.7–7.3 ppm, well resolved signals of the aromatic protons in EFl can be detected; the signal at $\delta = 2.6$ ppm, which disappears on deuteration, is attributed to the OH proton and the signal at $\delta = 2.45$ ppm to the $\equiv$C–H proton (*Figure 4a*). The spectrum of PEFl shows coalescence of the resonances of the aromatic protons, and several signals in the range 7–5.5 ppm, attributable to the backbone hydrogens. The large number of signals of almost equal intensity suggests that chain fragments may have different *cis–trans* sequences and may contain monomer units with tail to head, or tail to head–head to tail enchainments. The broad signal at $\delta = 2.05$ ppm, that disappears by D_2O treatment, can be attributed to

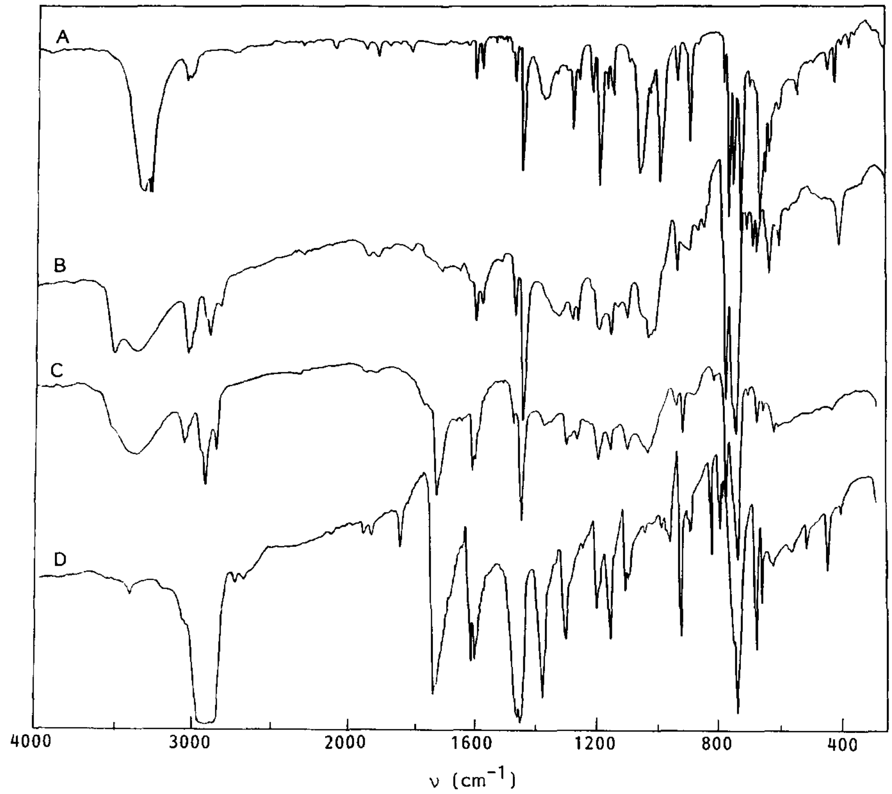

Figure 2 I.r. spectra: A, EFl; B, PEFl; C, modified PEFl; D, fraction eluted from the chromatography of modified or oxidized PEFl, corresponding to 9-fluorenone. Spectra A, B and C were obtained from films cast from CH_2Cl_2; spectrum D was obtained from nujol mull

OH proton resonance. The signals below 2 ppm are probably due to minor side products obtained in the polymerization reaction. These minor products are probably responsible for the lowering of the number average M_w determined by osmometric measurements. The ^{13}C n.m.r. spectrum of EFl was also studied by the attached proton test (APT) technique; *Figure 5a* shows the resonances of the aromatic carbons carrying hydrogens at $\delta = 129.8$, 128.6, 124.2 and 120.2 ppm. By comparison with literature data[27,28] they correspond to C_3, C_2, C_1 and C_4, respectively; the quaternary carbon atoms give the signals at $\delta = 146.5$ ppm (C_{10}), $\delta = 139.6$ ppm (C_{11}) and $\delta = 74.5$ ppm (C_9). The carbon atoms C_{12} and C_{13} give signals at 83.8 and 71.3 ppm, respectively[29]. If we compare the ^{13}C n.m.r. spectrum of the polymer (*Figure 5b*) with that of the monomer we can see that the C_1, C_2, C_3 and C_4 carbon atoms carrying hydrogens of the fluorenol pendent groups give signals almost at the same frequencies as the monomer; the increased number of observed signals (*Figure 5b*) can be correlated to a disordered morphology of the polymer chain. Several resonances are also observed in the range 145–150 ppm and 138–140 ppm (C_{10} and C_{11} carbon atoms of the pendent groups). By comparison with the ^{13}C n.m.r. spectrum of stereoregular PPA[22], the signals in the range 131.9–141.4 ppm (*Figure 5b*), which appear inverted in the APT spectrum, can be due to =CH carbons of the disordered polymer chain.

X.p.s. spectra. X.p.s. measurements have also been performed on EFl and PEFl. The monomer was found to be sensitive to X-ray radiation; in order to avoid decomposition, the sample was left under vacuum in the analysis chamber and then cooled with a liquid N_2 flux before and during the measurement. The C1s core level peak maximum is taken at binding energy (b.e.) value of 285.0 eV (as fixed to calibrate the energy scale[18]) with a full width at half maximum (f.w.h.m.) of 2.6 eV and with a shake-up satellite at $\Delta s \approx 7.3$ eV (*Figure 6A*). The O1s signal has a maximum at b.e. = 532.9 eV (f.w.h.m. ≈ 3.2 eV) (*Figure 6A′*) and the composition determined from the quantitative evaluation of atomic ratios is $C_{15}O_{1.5}$.

When the sample is heated up to room temperature the C1s signal becomes broad (f.w.h.m. ≈ 2.9 eV) with a tail towards higher b.e. values, where the signals of C=O are usually found[30]. Broadening of the O1s peak is also observed (f.w.h.m. ≈ 3.5 eV) with a slight asymmetry towards the lower b.e. values. X.p.s. measurements of a reference molecule C_6H_5–CO–CO–C_6H_5 have been also examined; the C1s core level spectrum exhibits one peak at 285.0, and a shoulder at ≈287.5 eV which is attributed to C=O groups. The O1s signal was found at 532.2 eV; the resulting atomic composition is $C_{12}C_2O_2$. These data, by comparison with the X.p.s. spectrum of EFl, indicate that the monomer decomposes at room temperature under X-ray radiation, giving a product containing C=O groups, probably fluorenone (see below).

The X.p.s. spectra of PEFl (obtained as a thin film cast from a CH_2Cl_2 solution onto a polished stainless steel probe) show the C1s peak at 285.0 eV (f.w.h.m. = 2.0 eV) with its shake-up satellite at $\Delta s \approx 7.4$ eV (*Figure 6B*). The signal is narrow; only a slight asymmetry towards higher b.e. values can be detected. The O1s signal has a maximum at 532.8 eV (f.w.h.m. = 2.3 eV); in this case a little asymmetry towards lower b.e. values (*Figure 6B′*) can also be observed. The atomic composition

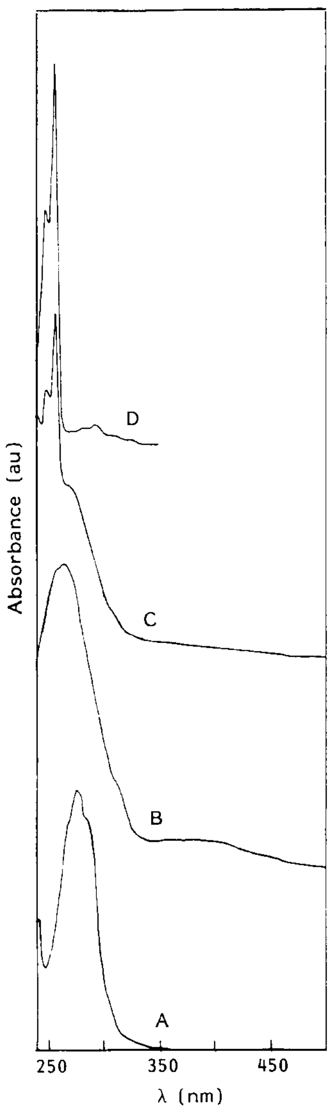

Figure 3 U.v. spectra (in $CHCl_3$): A, EFl; B, PEFl; C, modified PEFl; D, eluted chromatographic fraction (9-fluorenone)

evaluated from X.p.s. data gives $C_{15}O_{1.05}$, close to the calculated values. It is noteworthy that PEFl seems to be more stable than its monomer under X-ray radiation and that the repeat unit in the backbone is well preserved.

Investigations on the stability of PEFl in solution

One of the most important properties of polymers derived from monosubstituted acetylenes is their solubility in several organic solvents. Solutions of polymers can be mixed with solutions of doping agents: solid samples with an homogeneous distribution between the dopant and the polymer molecules can be obtained by evaporation of the solvent. Therefore we considered it of interest to investigate the stability of PEFl in various solvents by following modifications of the u.v. spectra with time. We found that the u.v. spectra of the polymeric solutions (PEFl in $CHCl_3$) undergo slow modifications changing the pattern of the absorption bands. New peaks appear at $\lambda = 250$ and 259 nm. Their intensity increases slowly with time. The spectrum of *Figure 3C* was taken after about 20 days. Analogous modifications in the optical spectra were observed for solutions of PEFl in THF and C_6H_6. The i.r. spectrum of the solid recovered after 20 days from the $CHCl_3$ solution of PEFl (modified PEFl) is given in *Figure 2C*: a strong band at $\sim 1700\,cm^{-1}$ indicates the formation of products containing C=O groups. The ^1H n.m.r. spectrum of the same solid product (*Figure 4C*) shows a multisignal feature in the range 8–7 ppm (aromatic protons) and signals of minor intensity in the range 6–4 ppm which, however, do not appear at the same resonance position as the backbone protons of pristine PEFl (compare *Figure 4b*). A new sharp signal is found at $\delta = 1.24$ ppm (CH_2 protons) with other small peaks at 2.0, 1.6 and 0.8 ppm, which partly disappear upon D_2O exchange.

The ^{13}C n.m.r. of modified PEFl is reported in *Figure 5c*. By comparison with the spectrum of pristine PEFl we can notice that the aromatic carbon atoms carrying hydrogen give three multiplets in the range 129–119 ppm, as for pristine PEFl. The signals attributed to the quaternary carbon atoms are almost unchanged. In the range of vinylic carbons only a signal at 134.66 ppm is

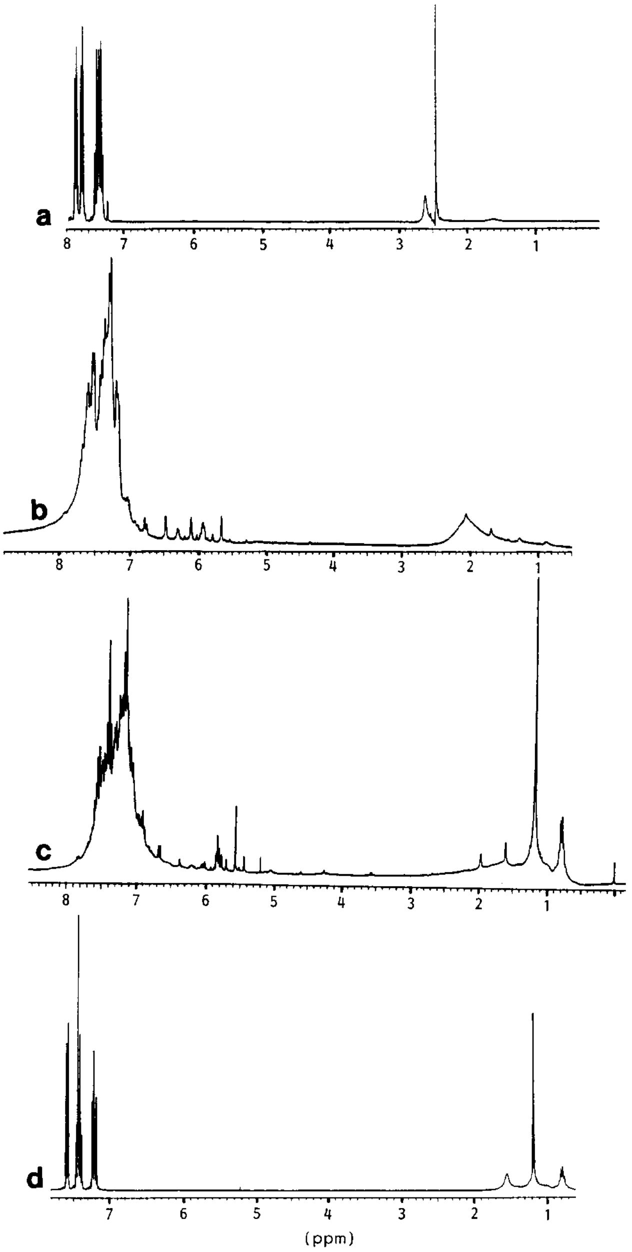

Figure 4 ^1H n.m.r. spectra (in $CDCl_3$, TMS internal standard): (a) EFl; (b) PEFl; (c) modified PEFl; (D) eluted chromatographic fraction (9-fluorenone)

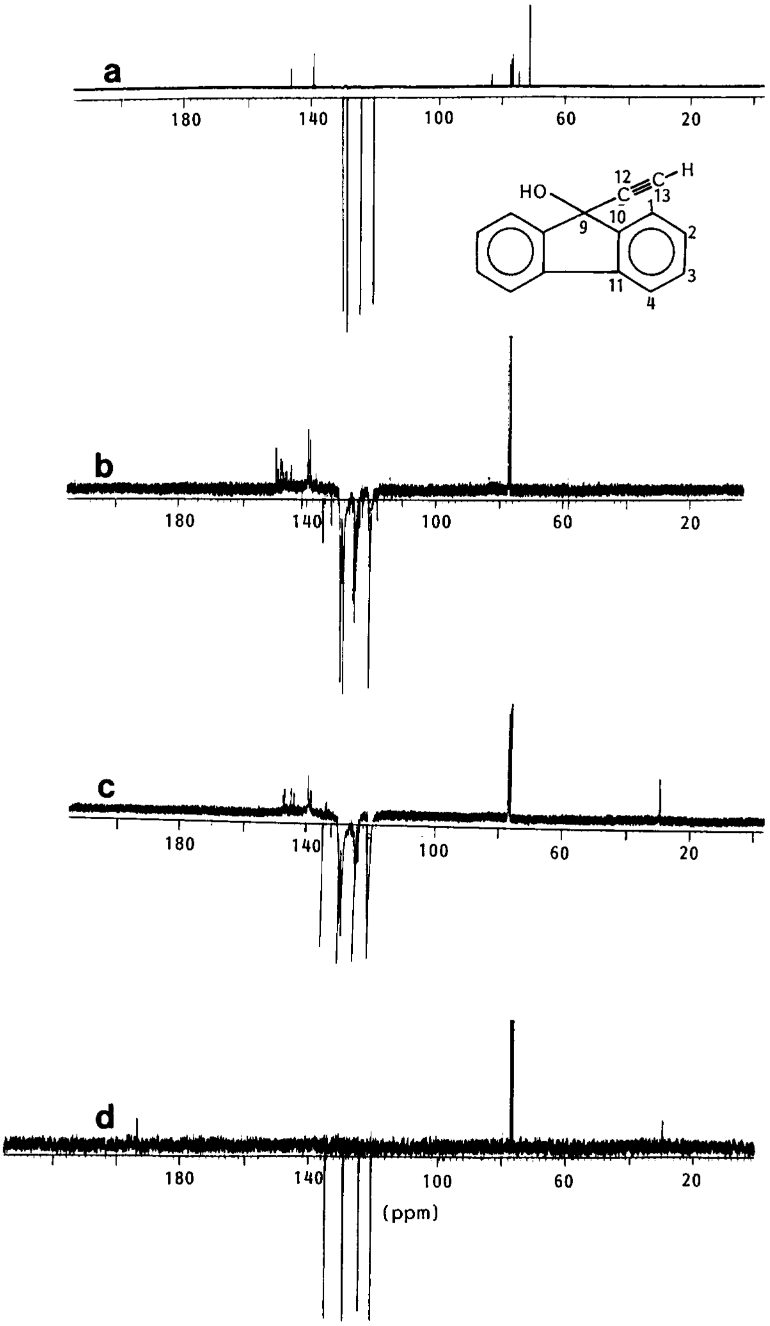

Figure 5 ^{13}C n.m.r. (APT) spectra (in $CDCl_3$): (a) EFl; (b) PEFl; (c) modified PEFl; (d) eluted chromatographic fraction (9-fluorenone)

more evident. A new signal at 29.67 ppm suggests the presence of CH_2 groups.

The molecular weight (osmometric) of the recovered solid (modified PEFl), starting from the material of M_w 2000 amu was 500 amu, indicating a partial degradation of the pristine polymer. A t.l.c. investigation confirmed that the solid was a mixture of products with increased oxygen content (C = 74.43%, H = 4.70%). Therefore in order to characterize the components of this mixture, oxidation reactions of EFl and PEFl were carried out with aqueous $KMnO_4$ (see Experimental). The obtained oxidation products and a sample of PEFl modified in solution were chromatographed on a SiO_2 column using $CHCl_3$ as the eluent. The first fractions of all the investigated samples exhibited the same u.v., i.r. and n.m.r. spectra, which are reported in *Figures 2D*, *3D*, *4d* and *5d*. By comparison with literature data[27,28,31,32] the spectra are consistent with those of fluorenone (see X.p.s. results) except for the signals at about 1.16 ppm (^1H) and 29.6 ppm (^{13}C) in the n.m.r. spectra. These signals are due to minor products formed in the decomposition and/or oxidation reactions, which are not separated from fluorenone by chromatography on SiO_2 if $CHCl_3$ is used as the eluent. However, if these fractions are further chromatographed on SiO_2 using benzene as eluent the signals at 1.16 ppm (^1H) and 29.6 ppm (^{13}C) disappear and the n.m.r. spectrum corresponds to that of 9-fluorenone.

Further fractions, obtained from oxidized and modified PEFl by elution with $CHCl_3$, have i.r. and n.m.r. spectra similar to those of the pristine polymer, indicating that the polymer undergoes only a partial decomposition even when it is treated with a strong oxidizing agent such as $KMnO_4$.

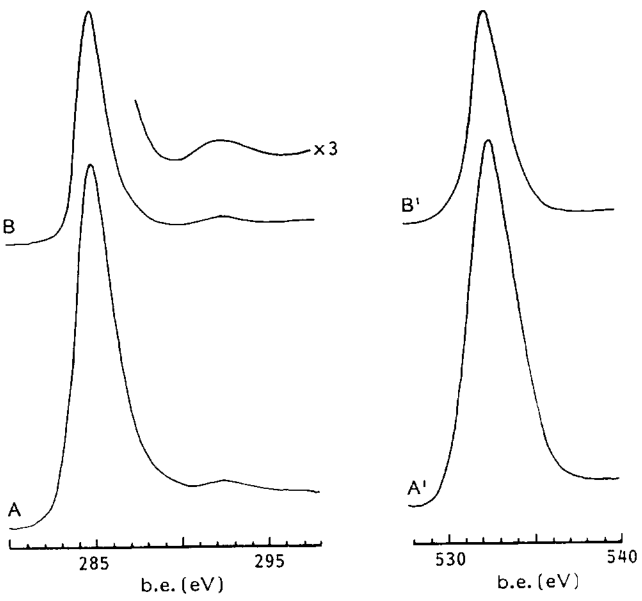

Figure 6 X.p.s. Cls core level spectra of: A, EF; B, PEFl. X.p.s. Ols core level spectra of: A', EFl; B', PEFl

Table 2 Resistance (R) of doped PEFl samples recorded in dry and in humid atmosphere

Dopant	R (Ω) dry	R (Ω) humid	R[a] (Ω) dry	R[a] (Ω) humid
I_2[b]	5×10^9	5×10^8	1×10^{12}	1×10^{12}
$FeCl_3$[b]	2×10^9	5×10^2	3×10^7	2×10^2
$SnCl_2$[b]	2×10^9	1×10^4	2×10^8	7×10^3
$NaBH_4$[b]	3×10^{10}	1×10^6	3×10^9	1×10^7
HCl[c]	5×10^{11}	1×10^6	8×10^{11}	2×10^5
H_2SO_4[c]	1×10^7	1×10^4	2×10^7	1×10^5
$HClO_4$[c]	2×10^6	1×10^3		

[a] Measurements performed on the same sample maintained at ambient conditions for 3 months
[b] Nominal doping percentage 50% w/w
[c] Nominal doping percentage: see Experimental

Electrical properties of doped PEFl

Influence of doping agents. Undoped PEFl is an insulator ($R = 10^{14}\,\Omega$) like the majority of pristine polyconjugated materials. Different dopants, however, increase its conductivity. The results are reported in *Table 2*. So as we have already observed for PPA[33], PEFl doped samples are stable in ambient conditions for long periods; their conductivity is dependent on the percentage of water vapour and increases by increasing the ambient humidity (*Table 2*). In *Figure 7* the variation of resistance for the $FeCl_3$ doped (50% w/w) PEFl sample previously dried under vacuum and introduced into a measurement chamber saturated with water vapour (~95% r.h.) is reported. The resistance decreases by ~3–4 orders of magnitude in ~30 min. This response to r.h. variations is reproducible for subsequent cycles on the same sample. For example, in *Figure 8* the measurements performed on a $FeCl_3$-doped PEFl sample are reported over a period of 80 h: points A and F show the resistance of the sample stored at laboratory ambient conditions; points B, D and G show the remarkable decrease of resistance occurring when the sample is transferred into a measurement chamber at ~95% r.h.; points C and E give the resistance of the sample dried under dynamic vacuum for ~16 h and stored in a dry atmosphere. Further measurements are currently in progress to explain the influence of humidity on the conductivity process.

X.p.s. measurements on I_2-doped PEFl. The I_2-doped polymers have been the subject of extensive investigations. The indentification of the doping species obtained from the charge-transfer reaction occurring between polymer and I_2 is not immediate. It seems accepted that the doping reaction leads to $I_2 + I_3^- \rightarrow I_5^-$ (or polyiodide species)[34–36], the equilibrium being more shifted towards one side or the other depending on the nature of the polymer[37,38] and/or the doping procedure[39].

X.p.s. measurements were performed on PEFl films cast from CH_2Cl_2 solutions on a stainless steel probe and exposed to I_2 vapours for 10 and 30 min at room temperature or for 60 min at 60°C (*Figure 9*). The $I3d_{5/2}$ core level spectra of the samples doped at room

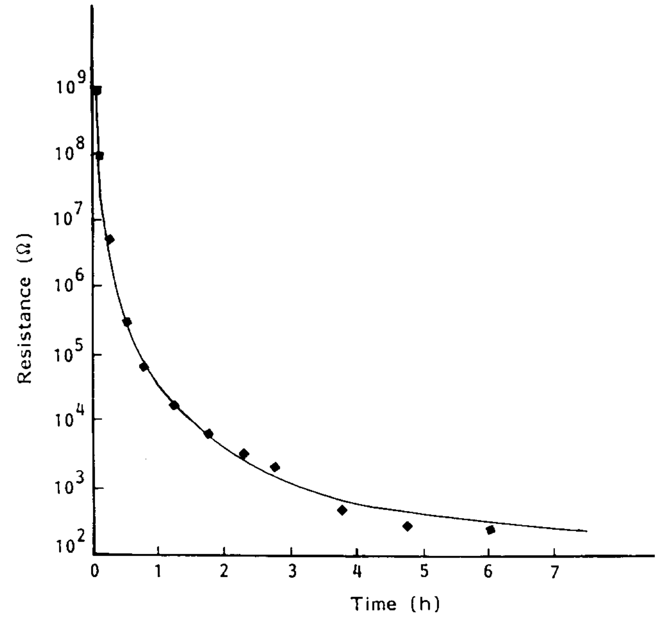

Figure 7 Resistance variations *versus* time of $FeCl_3$-doped PEFl when introduced into a measurement chamber at ~95% r.h.

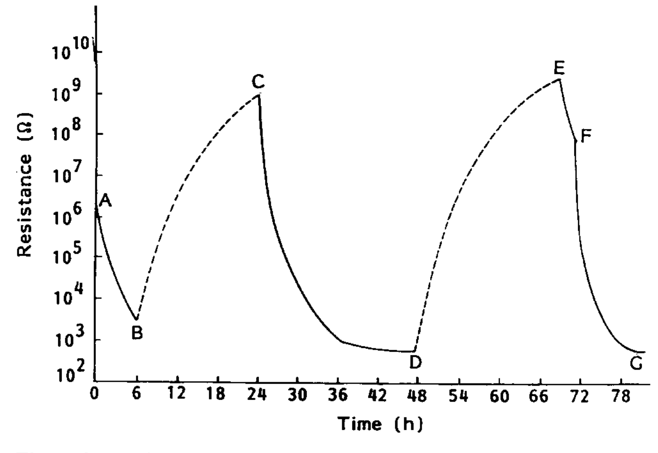

Figure 8 Resistance variations *versus* time of $FeCl_3$-doped PEFl exposed to: A, ambient conditions; B, D, G, ~95% r.h.; C, E sample dried under dynamic vacuum; F, ambient conditions. ——, Experimental measurements; – – –, predicted connections between points B–C and D–E

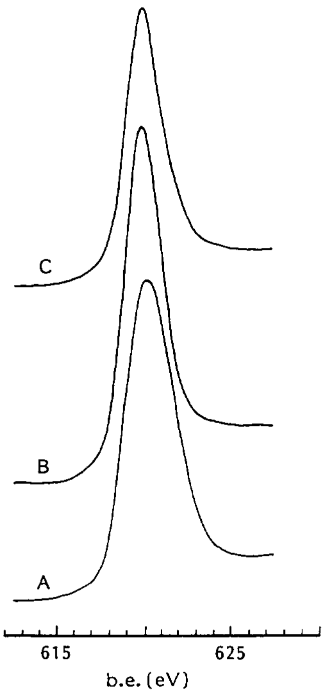

Figure 9 X.p.s. $I3d_{5/2}$ core level spectra of a PEFl film doped with I_2 vapours for: A, 10 min; B, 30 min; C, 60 min

temperature show composite signals with variable width (3.8–3.3 eV f.w.h.m.). One of the components can be found at 619.6–619.9 eV and the other can be found as a shoulder at higher b.e. values; the calculated ratios of the two components are also variable depending on the exposure time of the sample to I_2 vapour. In the case of the 10 min I_2-doped film, the ratio is roughly 1:1. Resuming the topics discussed about I_2-doped PPA films[18], the component at ~619.8 eV might be indicative of the presence of I_5^- while the component at higher b.e. values (~620.6 eV) should suggest the presence of I_2 segregated at the surface (this component is still present, although smaller, after pumping overnight). The I3d signal of the PEFl film doped for 60 min at 60°C is narrow (f.w.h.m. = 2.6 eV) with the maximum at 619.6 eV and with only a slight asymmetry towards higher b.e. values (*Figure 9*); I_5^- may thus be suggested as the predominant species, although this b.e. value is about 0.5 eV lower than that proposed for I_2-doped PPA[18]. The atomic composition of the last mentioned sample is $C_{15}O_{1.1}I_{0.49}$; this means one I_5^- for every 10 monomer units.

The C1s signals of doped PEFl samples are narrow (f.w.h.m. = 2.1 eV), centred at 285.0 eV (no shift with respect to undoped PEFl) and no or very small associated shake-up satellites are evident. The absence of carbon shake-up satellite has been associated with the enhancement of $\pi \rightarrow \pi^*$ transitions occurring upon doping[39]. The O1s signal is generally found at ~532.6 eV and at 533.1 eV in some cases its width is variable from 2.2 eV to 2.5–3.0 eV (f.w.h.m.). The broadening of the O1s signal may be due to the interaction of the samples with environmental humidity.

DISCUSSION

The most active catalysts reported here towards the polymerization of EFl are $[Rh(COD)Cl]_2$ and $[Pd(EFl)_2(PPh_3)_2]$. The Rh(I) complex proved to be a good catalyst in the synthesis of poly(monosubstituted) acetylenes[6,13,14,22] $(-CH{=}CR)_n$ with R = Ph, CH_2–NH–CH_2–Ph, $C_5H_4FeC_5H_5$; its reactivity towards acetylenes with R containing OH groups is also confirmed. It is noteworthy that the analogous [Rh(COD)im], which yielded PPA films[19], is completely ineffective towards EFl. The Pd(II) bis-acetylide complex is also very active, as expected owing to the presence of the metal-carbon σ-bonds[24], while the analogous Pt(II) catalyst shows lower reactivity and the Ni(II) monoacetylide does not give any reaction product. We should point out once more that, in the field of catalytic reactivity, it is difficult to confirm predictions: every system (catalyst–substrate) shows a peculiar behaviour.

PEFl is stable at normal ambient conditions. It is interesting that the polymer is more stable under X-ray radiation than the monomer, which is converted to fluorenone. PEFl is soluble in the most common organic solvents; only a slow decomposition takes place in solution, as reported earlier in this paper. The M_w measurements show that the polymer chains are not very long, in the range of 10 monomer units; however the osmometric method underestimates the real M_w.

The i.r. and n.m.r. spectra of PEFl suggest that the polymerization reaction runs through the opening of the triple acetylenic bond leading to a linear backbone of conjugated double bonds with R = $C_{13}H_9O$ as pendent groups. The presence of two bands at ~3540 and 3350 cm^{-1} (νOH) suggests that the OH group may be involved in interchain hydrogen bonds.

The ^1H and ^{13}C n.m.r. spectra indicate that PEFl has a low degree of stereoregularity, because of the high number of aromatic protons and ^{13}C signals with respect to the monomer, which indicate that the R groups are not in equivalent positions along the chain; the presence of multiplets in the range 7–5.5 ppm in the ^1H spectrum suggests that the backbone hydrogens may be located in different *cis–trans* sequences of the monomer units.

The stability investigations and oxidative reactions performed on PEFl and EFl show that the modifications of the polymer in solution lead mainly to the release of some of the pendent groups because 9-fluorenone was recovered in the chromatographed decomposition products and identified by the i.r., u.v. ^1H and ^{13}C n.m.r. spectra.

The resistance measurements performed on doped PEFl show that improvement of the electrical conductivity can be achieved up to ~10 orders of magnitude and that the doped samples maintain their properties for a long time (~3 months) without special storage conditions. The reversible response of the doped polymer to variations of r.h. is also interesting; this behaviour will be more extensively investigated with regard to interpreting the conductivity mechanism and the application of this system as a gas sensor.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support of CNR-Progetto finalizzato 'Materiali Speciali per Tecnologie Avanzate' (Italy).

REFERENCES

1 Skotheim, T. A. (Ed.) 'Handbook of Conducting Polymers', M. Dekker, New York, 1986

2 Garnier, F., Horowitz, G. and Fichon, D. *Synth. Met.* 1989, **28**, C705

3 Baughman, R. H. and Shacklette, L. W. *Phys. Rev. B* 1989, **39**, 5872 and references therein

4 Feast, W. J. and Friend, R. H. *J. Mater. Sci.* 1990, **25**, 3796

5 Kang, E. T., Ehrlich, P., Bhatt, A. P. and Anderson, W. A. *Macromolecules* 1984, **17**, 1020

6 Furlani, A., Napoletano, C., Russo, M. V., Camus, A. and Marsich, N. *J. Polym. Sci. A* 1989, **27**, 75

7 Chang, T. L., Holzknecht, L. J., Mark, H. B. Jr, Ridgway, T. and Zimmer, H. *J. Polym. Sci. A* 1989, **27**, 989

8 Petit, M. A., Soum, A. H., Leclerc, M. and Prud'homme, R. E. *J. Polym. Sci. B* 1987, **25**, 423

9 Lindgren, M. and Lee, H. S. personal communication

10 Lee, H. S., Lindgren, M., Yang, W., Tabata, M. and Yokota, K. *Polym. Prepr. Jpn* 1989, **38**(7), 2274

11 Neher, D., Wolf, A., Bubeck, C. and Wegner, G. *Chem. Phys. Lett.* 1989, **163**(2,3), 116

12 Furlani, A. and Russo, M. V. *Appl. Organomet. Chem.* 1990, **4**, 319 and references therein

13 Furlani, A., Paolesse, R., Russo, M. V., Camus, A. and Marsich, N. *Polymer* 1987, **28**, 1221

14 Polzonetti, G., Faruffini, V., Furlani, A. and Russo, M. V. *Synth. Met.* 1988, **25**, 375

15 Cianciusi, A. M., Furlani, A., La Ginestra, A., Russo, M. V., Palyi, G. and Vizi-Orosz, A. *Polymer* 1990, **31**, 1568

16 Furlani, A., Napoletano, C., Paolesse, R. and Russo, M. V. *Synth. Met.* 1987, **21**, 337

17 Furlani, A., Russo, M. V., Polzonetti, G., Martin, K., Wang, H. H. and Ferraro, J. R. *Appl. Spectr.* 1990, **44**(2), 331

18 Polzonetti, G., Furlani, A., Russo, M. V., Camus, A. M. and Marsich, N. *J. Electron Spectr. Relat. Phenom.* 1990, **52**, 581

19 Camus, A., Marsich, N., Furlani, A. and Russo, M. V. unpublished results

20 Hartley, F. R. *Organomet. Chem. Rev. A* 1970, **6**, 119

21 Carusi, P. and Furlani, A. *Gazz. Chim. Ital.* 1980, **110**, 7

22 Furlani, A., Napoletano, C., Russo, M. V. and Feast, W. J. *Polym. Bull.* 1986, **16**, 311

23 Furlani, A., Bicev, P., Carusi, P. and Russo, M. V. *Polym. Lett.* 1971, **9**, 19

24 Bicev, P., Furlani, A. and Russo, M. V. *Gazz. Chim. Ital.* 1980, **110**, 25

25 Matsuda, T., Ohtori, T. and Higashimura, T. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* 1979, **20**, 731

26 Avram, M. and Mateescu, G. D. in 'Infrared Spectra of Organic Compounds', Wiley Interscience, New York, 1972, p. 208

27 Hirayama, M. and Ohhata, H. *Bull. Chem. Soc. Jpn* 1987, **60**, 2751

28 Drake, J. A. G. and Jones, D. W. *Spectrochim. Acta* 1980, **36A**, 23

29 Carusi, P., Cerichelli, G., Furlani, A., Russo, M. V. and Suber, L. *Appl. Organomet. Chem.* 1987, **1**, 555

30 Chilkoti, A., Ratner, B. D. and Briggs, D. *Chem. Mater.* 1991, **3**, 51

31 Hirayama, M., Suzuki, H. and Ohhata, H. *Chem. Lett.* 1987, 413

32 Simpson, W. W. (Ed.) 'The Sadtler Handbook of Infrared Spectra', 'The Sadtler Handbook of Ultraviolet Spectra', Sadtler Research Laboratories, Sadtler Heyden, 1978

33 Furlani, A., Russo, M. V., Cianciusi, A. M., Bruno, F., Mercuri, R., Paoletti, A. and D'Amico, A. *Chemtronics* 1988, **3**, 239

34 Hsu, S. L., Signorelli, A. J., Pez, G. P. and Baughman, R. H. *J. Chem. Phys.* 1978, **69**(1); 106

35 Salaneck, W. R., Thomas, H. R., Bigelow, R. W., Duke, C. B., Plummer, E. W., Heeger, A. J. and MacDiarmid, A. G. *J. Chem. Phys.* 1980, **72**(6), 3674

36 Murthy, N. S., Miller, G. G. and Baughman, R. H. *J. Chem. Phys.* 1988, **89**(4), 2523

37 Ferraro, J. R., Furlani, A. and Russo, M. V. *Appl. Spectrosc.* 1987, **41**(5), 830

38 Petit, M. A., Soum, A. M., Leclerc, M. and Prud'homme, R. E. *J. Polym. Sci. B, Polym. Phys.* 1987, **25**, 423

39 Salaneck, W. R. *Contemp. Phys.* 1989, **30**(6), 403