Polymerization of *p*-diethynylbiphenyl via oxidative or catalytic reactions

A. Bolasco†, F. Chimenti†, A. Frezza*, A. Furlani*, G. Infante*, E. Muraglia*, G. Ortaggi*, G. Polzonetti*, M. V. Russo*‡ and G. Sleiter*
**Dipartimento di Chimica; †Dipartimento di Studi di Chimica e Tecnologia delle Sostanze Biologicamente Attive, University 'La Sapienza', P.le A. Moro 5, 00185 Rome, Italy*
(*Received 22 May 1991; accepted 24 July 1991*)

Oxidative and catalytic polymerizations of DEBP (*p*-diethynylbiphenyl) were investigated. The characterization of the reaction products, ox-PDEBP and c-PDEBP (originating from the oxidative and catalytic reactions respectively), was performed by means of i.r., XPS and t.g.–d.t.a. techniques. The different behaviour of ox-PDEBP and c-PDEBP in the presence of oxygen and humidity was examined. The variations of the electrical properties upon doping with $FeCl_3$ and I_2 are also reported.

(**Keywords: diethynylbiphenyl; polymerization; catalytic; oxidative**)

INTRODUCTION

Diacetylenes have been the object of great interest and extended research in recent years because, upon polymerization, they can give rise to extended conjugated π-systems. Polyacetylenes have physical and chemical properties[1] which make them interesting materials for use in electronics, optics, biophysics[2], biochemistry and time–temperature devices[3].

From the polymerization of diacetylene monomers, different polymers can be obtained, depending on the relative position of the two triple bonds in the monomer. When the triple bonds are conjugated, as in butadiyne or its derivatives, $R{-}C{\equiv}C{-}C{\equiv}CH(R)$ ($R{=}C_2H_5$, C_6H_5, $CH_3C_6H_4$, SO_3CH_2), highly crystalline polymers, showing specific electrical properties, can be obtained[4–9]. However, when the two triple bonds are isolated by an aliphatic chain, $HC{\equiv}C{-}(CH_2)_n{-}C{\equiv}CH$, only catalytic polymerization can give a polyacetylene-like polymer, with $(CH_2)_n{-}C{\equiv}CH$ pendent groups along the chain, since by oxidative polymerization no polymer with extended delocalization of the π-systems can be obtained. Crosslinked bonds between different chains can occur in such polymeric systems[10–12]. In this group of diynes a specific monomer widely used is 1,6-heptadiyne, $HC{\equiv}C{-}(CH_2)_3{-}C{\equiv}CH$, which was converted by Gibson *et al.*[13] into a polymer with a backbone similar to polyacetylene.

The third class of diacetylenes concerns molecules with an aromatic system inserted between the two triple bonds, which are therefore suitable for the synthesis of extended π-conjugated polymers. Many investigations have been carried out on the oxidative polymerization of these monomers[14–19], and electro-initiated[20] and palladium-catalysed[21] reactions of *p*-diethynylbenzene have recently been reported.

The present authors have extensively investigated the oxidative polymerization of aromatic and heteroaromatic diethynyl derivatives and have characterized the undoped and iodine-doped polymers[22,23]. Poly(*p*-diethynylbenzene) was used for the preparation of an ion-selective electrode and urease enzyme sensor[24].

This paper reports the results of an investigation on the oxidative and catalytic polymerization of *p*-diethynylbiphenyl (DEBP). This molecule was chosen because of the possibility of building more rigid chains with extended π-delocalization and to compare the influence of phenyl and biphenyl rings on the conjugated systems. Moreover, the effects of doping may be strikingly different, and the polymer may be subjected to hyper-crosslinking which may influence the physical properties of this material, especially Young's modulus, thermal stability and hardness.

EXPERIMENTAL

Methods and instruments

I.r. spectra were recorded on a Perkin-Elmer 580B spectrometer as nujol mulls, and u.v. spectra on a Perkin-Elmer Lambda 5 spectrometer. Molecular weights were determined by a Knauer Osmometer model 11 at 30°C, using $CHCl_3$ as the solvent.

Melting points were measured with a Kofler apparatus. Elemental analyses were made by the Laboratorio di Microanalisi, Università di Pisa, Italy. Resistance measurements were performed at ambient conditions by a Keithley 616 digital electrometer on pressed pellets (thickness ≈ 0.1 cm, diameter ≈ 1.3 cm) prepared in a Specac P/N 150 hydraulic press at 10 tons.

Simultaneous t.g.–d.t.a. curves were recorded with a Stanton 801 STA Thermoanalyzer, using Pt crucibles, Pt/(Pt, 13% Rh) thermocouples and heating rates of 5 K min^{-1} in an air stream.

---

‡To whom correspondence should be addressed

0032-3861/92/143049-06
© 1992 Butterworth-Heinemann Ltd.

The X-ray photoemission (XPS) experiments were carried out on a VG ESCA 3 MK1 instrument, using Al K$\alpha_{1,2}$ radiation ($h\nu = 1486.6$ eV), with a typical vacuum in the analysis chamber of 2×10^{-9} Torr. The samples were deposited as thin powder films on to a polished stainless steel probe. All the spectra were energy-referenced to the C 1s photoionization peak, to which was assigned a binding energy of 285.0 eV. Quantitative evaluation of atomic ratios in the XPS sampling layer was achieved by analysis of the XPS signal intensity, using Scofield's atomic cross-section values[25].

Materials

The following symbols are adopted in the text: DEBP = 4,4′-diethynylbiphenyl; COD = *cis,cis*-cyclooctadiene; im = imidazole; PDEBP = poly(4,4′-diethynylbiphenyl).

All solvents were reagent-grade and distilled over $CaCl_2$ or sodium.

The monomer (DEBP) was prepared by a published method[26], which employs the reaction of 4,4′-dibromobiphenyl with trimethylsilylacetylene in the presence of CuI, Et_2NH and $[(Ph_3P)_2PdCl_2]$. The monomer was also prepared by the original procedure of the present authors[22], which is based on the halogenation of 4,4′-diacetylbiphenyl with phosphorus pentachloride, followed by elimination of HCl with potassium *tert*-butoxide in *tert*-butyl alcohol.

$[Rh(COD)Cl]_2$, a commercial product (Fluka), and the complex 1 isolated from the reaction between $[Rh(COD)Cl]_2$ and imidazole, whose structure is tentatively reported as [Rh(COD)im] since it is still under investigation[27], were used as polymerization catalysts. $[Pt(PPh_3)_2Cl_2]$ and $[Pd(PPh_3)_2Cl_2]$ were prepared according to published methods[28]. The new complexes, $[M(PPh_3)_2(DEBP)_2]$ (M = Pd, Pt) were prepared by reacting the corresponding bis-triphenylphosphine dichlorides with the monomer (DEBP) by the method reported for the synthesis of similar ethynyl complexes[29]. $[Pt(PPh_3)_2(DEBP)_2]$ (A) is slightly soluble in benzene and chloroform; $[Pd(PPh_3)_2(DEBP)_2]$ (B) is slightly soluble in chloroform but insoluble in most organic solvents. A and B do not melt up to 270°C. The complexes were characterized by elemental analysis and ultra-violet and infra-red spectroscopy.

Complex A: calc. for $PtP_2C_{68}H_{48}$: C 72.91 wt%, H 4.29 wt%; found: C 71.35 wt%, H 4.36 wt%. I.r. bands (cm^{-1}): 3300, 2100. U.v. ($CHCl_3$): $\lambda_{max} = 369$ nm. Molecular weight (osmometric): 1200 (calc. 1119).

Complex B: calc. for $PdP_2C_{68}H_{48}$: C 79.20 wt%, H 4.46 wt%; found: C 79.49 wt%, H 4.23 wt%. I.r. bands (cm^{-1}): 3300, 2100. U.v. ($CHCl_3$): $\lambda_{max} = 340$ nm.

Polymerization reactions

Oxidative polymerization. All operations were performed while bubbling oxygen through the reaction mixture. 0.2 mmol of CuCl in pyridine (20 ml) were vigorously stirred at room temperature for 5 min. DEBP (4.9 mmol) was then added and the temperature was raised to 65°C. After 3 h the light-yellow polymer powder (ox-PDEBP) was filtered, washed in turn with water, a solution of aqueous HCl in MeOH, water, MeOH, petroleum ether (b.p. 30–50°C), and dried under vacuum.

Catalytic polymerization.

(1) The monomer (DEBP) (500 mg), the catalyst (catalyst/monomer ≈ 1/100 molar ratio) and the cocatalyst (1 ml of 0.2 M NaOH in methanol) in 15 ml of benzene were refluxed for various times as reported in *Table 1*. The polymer, c-PDEBP, precipitated from the reaction solution as brown powder, was filtered off, washed with petroleum ether and dried under vacuum.

(2) The polymerization was also performed thermally by simply refluxing for 2 h a solution of the monomer (500 mg) in 10 ml of chloroform and 20 ml of paraffin oil (used to enhance the reaction temperature). The final product, t-PDEBP, was worked up as in (1).

(3) Films were formed by spreading on a flat glass vessel the catalyst (10 mg) dissolved in $CHCl_3$ (2 ml) and the monomer (100 mg); upon slow evaporation of the solvent, a brittle, brown film was obtained.

Doping procedure

0.1 g of PDEBP and 0.1 g of iodine or ferric chloride (nominal 50 wt%) were suspended in 20 ml of tetrahydrofuran and stored at room temperature for 24 h. The solvent was removed under vacuum and the doped samples were ground in a mortar and pressed into pellets for the resistance measurements.

RESULTS AND DISCUSSION

A brief comment is necessary about the two methods used for the preparation of 4,4′-diethynylbiphenyl. One involves mixing of 4,4′-dibromobiphenyl with a slight excess of trimethylsilylacetylene in the presence of catalytic amounts of bis[triphenylphosphine] palladium dichloride and copper(I) iodide in diethylamine[26]. The other starts from 4,4′-diacetylbiphenyl, using phosphorus pentachloride followed by potassium *tert*-butoxide in *tert*-butyl alcohol[22]. It is of interest that the reaction of 4,4′-diacetylbiphenyl with PCl_5 led, after chromatography on alumina with benzene as eluent, to the isolation of 4,4′-bis(α-chlorovinyl)biphenyl as white

Table 1 Polymerization reactions of DEBP

Catalyst	$[Rh(COD)Cl]_2$	$[Rh(COD)Cl]_2$	[Rh(COD)im]	$[Pd(PPh_3]_2Cl_2]$	$[Pd(PPh_3]_2Cl_2]$	$[Pd(PPh_3]_2(DEDP)_2]$		
Cocatalyst	NaOH	NaOH		NaOH	NaOH		Oxidative	Thermal
Solvent	C_6H_6[a]	C_6H_6	$CHCl_3$	C_6H_6	C_6H_6	C_6H_6	C_5H_5N	$CHCl_3$ paraffin oil
Time	5 min	5 min	12 h	7 h	20 h	24 h	3 h	2 h
Yield (wt%)	100	100	90	40	85	50	95	90

[a] Solvent distilled over Na; reaction performed in dry N_2

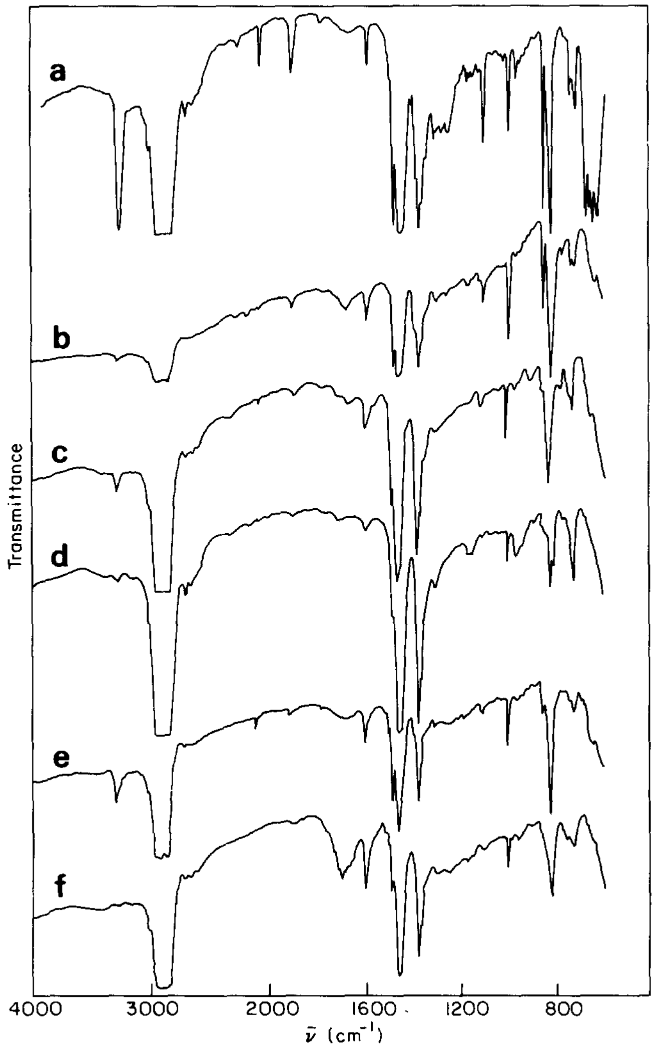

Figure 1 Infra-red spectra (nujol mulls): (a) DEBP; (b) ox-PDEBP; (c) c-PDEBP (Rh catalyst); (d) c-PDEBP ([Pd(PPh$_3$)$_2$Cl$_2$] catalyst); (e) c-PDEBP ([Pd(DEDP)$_2$(PPh$_3$)$_2$] catalyst); (f) t-PDEBP (thermal polymerization)

powder, m.p. 174–176°C, which is converted to 4,4′-diethynylbiphenyl by treatment with potassium *tert*-butoxide.

The polymerization reactions are summarized in *Table 1*. Most of the experiments were performed with [Rh(COD)Cl]$_2$ as active catalyst in the presence of NaOH as cocatalyst; with this complex the conversion of the monomer is complete in 5 min, while [Rh(COD)im], which was found to give free-standing films of polyphenylacetylene[27], is less active. c-PDEDP obtained via the catalytic route is insoluble in most common organic solvents; it can be purified from the catalysts, unreacted monomer and reaction solvent by treatment with hot benzene or petroleum ether. Surprisingly, the elemental analysis of c-PDEBP synthesized in the presence of catalysts shows carbon contents in the range 75–87 wt% and hydrogen contents of 4.1–4.8 wt%. Significant amounts of oxygen are always present, even when the polymerization reactions are carried out in a dry nitrogen atmosphere; this indicates rapid, immediate interaction with the environment by adsorption of water and/or oxygen. Similar behaviour was previously found by other authors for the polymer obtained by catalytic polymerization of 1,6-heptadiyne[13].

The polymer obtained by oxidative polymerization is a yellow powder, with an elemental analysis in good agreement with the calculated values (for $C_{16}H_{10}$: calc., C 95.45 wt%, H 4.55 wt%; found, C 93.22 wt%, H 4.01 wt%); it is infusible and insoluble in most organic solvents.

Thermal polymerization effects complete conversion of the monomer into the polymer, a brown, infusible and insoluble solid. Pd(II) complexes give good yields of c-PDEBP in 24 h under reflux in the presence of the cocatalyst. In contrast, Pt(II) complexes appear to exert little catalytic effect, since small amounts of PDEBP are formed even after 3–4 days of reflux.

I.r. spectra

Figure 1 shows the spectra of the monomer (a) and the polymers (b–f). Differences in the spectral patterns and in the relative intensities of the bands are observed for c-PDEBP obtained by different routes. The i.r. spectrum of ox-PDEBP (b) shows weak bands at 3300 (ν $\equiv$C–H) and 2200, 2150, 2100 (ν C$\equiv$C) cm^{-1} attributed to C$\equiv$C–H chain ends and to C$\equiv$C bonds of the rodlike polymeric backbone. Although ox-PDEBP is obtained by bubbling oxygen through the reaction mixture, only a weak broad band is observed at 1680 cm^{-1}, indicating the presence of only a small number of C=O groups formed during the oxidative reaction. Since this band is completely absent in poly(diethynylbenzene), the view seems to be supported that the larger the degree of conjugation, the larger the facility of oxidation of the triple bonds. The bands in the range 1100–700 cm^{-1} follow the spectral pattern of the monomer, while in the range 700–600 cm^{-1} no significant bands appear. PDEBP obtained in the presence of Rh(I) catalysts shows characteristic i.r. bands (*Figure 1c*) at 3300 and 2100 cm^{-1}, enhanced in intensity with respect to the bands of ox-PDEBP, suggesting that the polymerization occurs through the opening of one triple bond, leading to a linear chain of conjugated double bonds $[\text{–CH=CR–}]_n$ with the R = p-C_6H_4-p-C_6H_4–C$\equiv$CH moiety as a pendent group. Modifications of band intensity are also observed in the range 900–700 cm^{-1}. Broad bands at 3000–3600 cm^{-1} and 1600–1700 cm^{-1} are observed when the samples are exposed to the air, and disappear after warming under vacuum.

Figure 1(d–e) shows the spectra of c-PDEBP prepared in the presence of Pd(II) complexes, which appear similar to that of c-PDEBP obtained from Rh(I) complexes (*Figure 1c*): only enhancement of the bands at 970 and 720 cm^{-1} is observed for the polymer synthesized with [Pd(PPh$_3$)$_2$Cl$_2$]. The i.r. spectrum of t-PDEBP (thermal reaction) (*Figure 1f*) shows no bands at 3300 and 2100 cm^{-1}, which indicates enhancement of the polymer length and/or crosslinking between the pendent groups. A broad moderate band at 1700 cm^{-1} suggests the presence of C=O groups formed upon oxidation.

Thermal analysis

The d.t.a.–t.g. measurements performed in air on ox-PDEBP and c-PDEBP exhibit different trends. The t.g. analysis indicates good stability of ox-PDEBP up to ≈200°C (*Figure 2a*). Above that temperature an increase in weight of ≈6% is observed due to oxidation reactions of the polymer, which undergoes oxidative degradation at temperatures above 350°C.

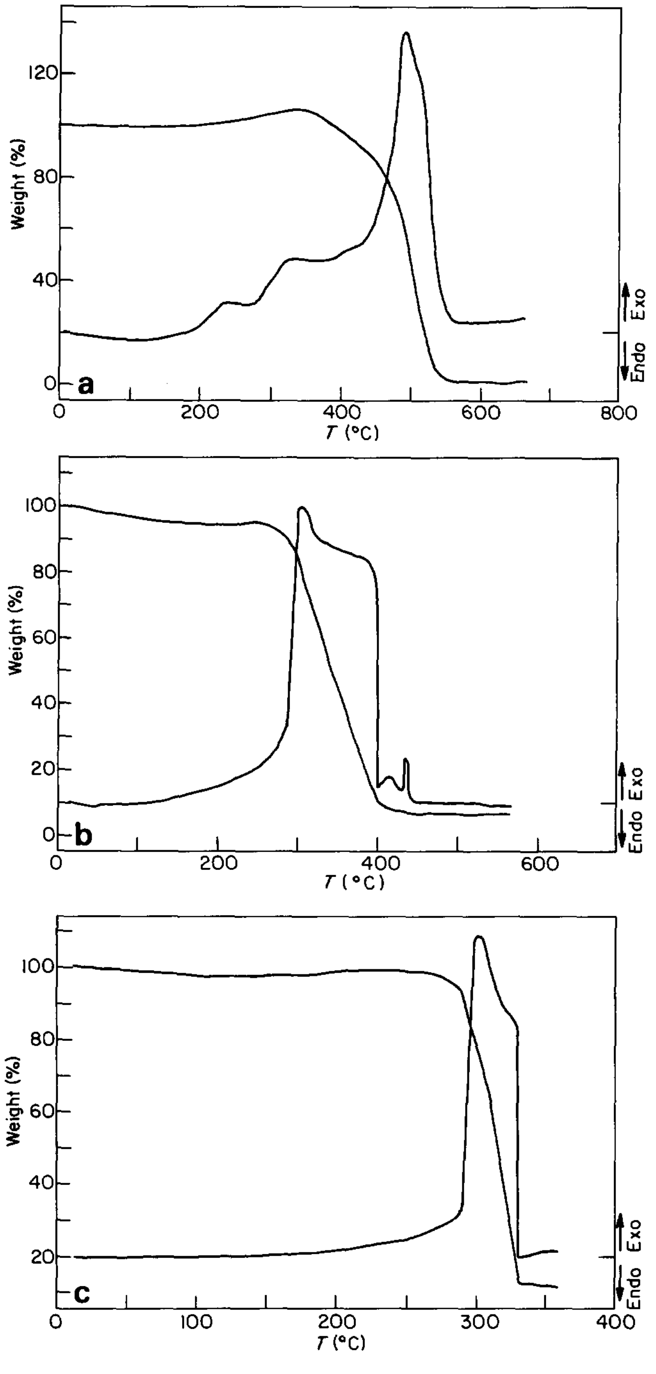

Figure 2 T.g.–d.t.a. curves: (a) ox-PDEBP; (b) c-PDEBP (Rh catalyst); (c) c-PDEBP (Rh catalyst, reaction performed under dry N_2 atmosphere)

Thermogravimetric curves of two samples of c-PDEBP are reported in *Figure 2*(*b*) and (*c*). In *Figure 2*(*b*) a gradual weight loss is observed, starting from ≈50°C. The c-PDEBP sample examined was prepared and maintained in air before the t.g. analysis. The observed weight loss of ≈6% can therefore be correlated with the oxygen content determined by elemental analysis and attributed to the presence of adsorbed water in the sample. *Figure 2*(*c*) shows the t.g. analysis of a sample prepared and maintained in a dry atmosphere. In this case the weight loss is lower, although not absent; handling of the sample cannot completely avoid interaction with humidity. A slight increase in weight is observed at temperatures above 180–200°C, as for the ox-PDEBP, but the uptake of oxygen is smaller. A drastic weight loss occurs at temperatures above 280°C, owing to an exothermic decomposition reaction.

The results indicate good thermal stability of both types of PDEBP; a difference in oxidation reactivity between ox-PDEBP and c-PDEBP is evident.

XPS measurements

Further characterization of the polymer was attempted by using the XPS technique. The C 1s core-level spectrum of ox-PDEBP (*Figure 3a*) is composite and shows the signal maximum of the main peak centred at 285.0 eV on the binding energy scale with a component at ≈288.0 eV and a full width at half-maximum (FWHM) of 2.8 eV; a similar pattern of the C 1s band (285.0 and 287.8 eV) is found for the reference compound C_6H_5–CO–CO–C_6H_5.

The C 1s shake-up satellite signal is found at $\Delta s \approx 7$ eV from the main peak; this is attributed to the presence of polymeric unsaturation or aromatic structures[30]. The O 1s signal is broad (FWHM ≈ 4 eV) with the maximum at 533.3 eV (*Figure 3b*); the calculated atomic ratio is C:O ≈ 1:0.025, in agreement with elemental analysis. It is possible that the breadth is due to signal components corresponding to different oxygen-containing groups: C=O of the reference compound gives the O 1s signal at 532.2 eV, while for adsorbed H_2O the value 533.5 eV is obtained; for the C–O–C group a value of 533.6 eV is reported in the literature[31]. Annealing of the sample to 220°C (under ultra-high vacuum) leads to a decrease in the C 1s and O 1s signal intensities, but the atomic ratio C:O remains unchanged (1:0.02). It is difficult to be certain (the breadth of the O 1s signal may also be due to solid-state effects, because the measurements were performed on powders); the results may indicate the presence of carbonyl groups, which are also evidenced by the i.r. spectra, and ether or hydroxy moieties in the polymer are also suggested. The interaction of polypyrrole with oxygen or water, resulting in the introduction of carbonyl groups into polymer chains, has been reported recently[32,33].

The C 1s signal of c-PDEBP (*Figure 3c*) is narrower (FWHM = 2.7 eV) than that of ox-PDEBP, centred at 285.0 eV, and no evident asymmetry, suggesting the presence of C=O groups, can be detected; the shake-up satellite is found at $\Delta s = 6.6$ eV from the main peak. The O 1s peak is found at 533.0 eV (FWHM = 3.6 eV) (*Figure 3d*). Evaluation of the atomic ratio gives

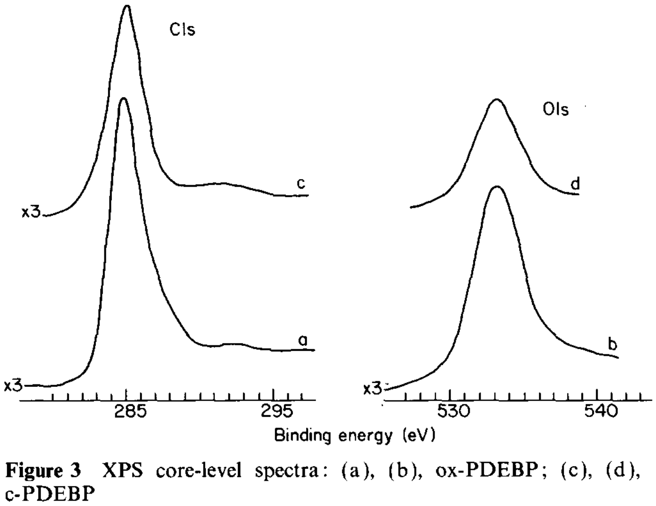

Figure 3 XPS core-level spectra: (a), (b), ox-PDEBP; (c), (d), c-PDEBP

C:O ≈ 1:0.052, i.e. about double the oxygen content with respect to ox-PDEBP, in agreement with the elemental analysis of c-PDEBP.

The position and FWHM of the O 1s peak are almost the same for both types of PDEBP. The absence of a shoulder in the C 1s peak of c-PDEBP, however, seems to exclude the presence of C=O groups formed in the interaction between the polymer and the atmosphere. In the i.r. spectra of c-PDEBP no bands at the characteristic C=O stretching frequencies are observed. The oxygen XPS signal in the c-PDEBP samples could be due to adsorbed water, as is suggested also by the i.r. spectra, showing broad bands in the region 3600–3300 cm^{-1}. It is surprising however that adsorbed water should be bonded to the polymer so strongly, because it ought to be eliminated under the high vacuum of the spectrometer chamber. The presence of C–O–C or C–OH groups cannot be excluded.

Electrical properties

The measured resistance (R) of both undoped ox-PDEBP and c-PDEBP samples was $\approx 10^{12}\,\Omega$. Doping with $FeCl_3$ or I_2 (50 wt%) in THF can be considered heterogeneous because of the insolubility of PDEBP, and is therefore presumably less effective than homogeneous doping, if the results and the considerations reported for PPA[34] can be reasonably extended to other systems. However, upon doping with $FeCl_3$ a resistance decrease of about seven ($R \approx 6 \times 10^5\,\Omega$) or nine ($R \approx 2 \times 10^3\,\Omega$) orders of magnitude can be obtained for the c-PDEBP and ox-PDEBP samples respectively. Doping with iodine produces a remarkable decrease in resistance for c-PDEBP obtained from $[Pd(PPh_3)_2(DEDP)_2]$ ($R \approx 3 \times 10^4\,\Omega$) and from thermal polymerization ($R \approx 6 \times 10^4\,\Omega$); in the other cases iodine doping seems to be less effective. The reason for this behaviour has not yet been elucidated, as apparently the structure of c-PDEBP is the same whatever the polymerization catalyst, but different from the structure of ox-PDEBP, which is poorly conductive upon iodine-doping ($R \approx 1 \times 10^8\,\Omega$).

CONCLUSIONS

PDEDP samples prepared by oxidative or catalytic reactions show small differences in their i.r. spectra which are not sufficient to elucidate the real polymer structure: the bands at 3300 and 2100 cm^{-1} give evidence of C≡C–H moieties that may be present either as chain-ending groups, assuming a rodlike backbone in ox-PDEBP, or as a part of the pendent groups p-C_6H_4–p-C_6H_4–C≡CH in the conjugated double-bond polymer backbone of c-PDEBP. However, the expected difference in the structure of the two polymers can be inferred from their reactivity towards oxygen and moisture.

Ox-PDEBP gives good elemental analyses and is stable in air. Only at temperatures above 200°C does it exhibit a tendency to react with oxygen and a slight weight increase is observed. Oxidative degradation takes place at temperatures above 350°C, indicating a good thermal stability of the polymer (even in air). The C 1s and O 1s XPS core-level spectra confirm that in the oxidative polymerization, carbonyl groups are formed to a small extent.

C-PDEBP on the other hand exhibits a strong tendency to absorb moisture from the atmosphere. In fact, elemental analysis indicates the presence of oxygen in the samples. The thermal analysis of c-PDEBP confirms the moisture absorption from the environment. A weight loss is observed in the range 50–120°C which is very low for the samples prepared and maintained in a dry atmosphere, and corresponds to the amount of oxygen found by elemental analysis. XPS measurements confirm the analytical and t.g. data.

It is not clear why the surface adsorbed water is not completely released under high vacuum during X-radiation, but other polymers[34] show the same behaviour, which is still under investigation.

Doping with $FeCl_3$ leads to a decrease in electrical resistance for both the polymers, being more effective for ox-PDEBP, while iodine doping gives better results for c-PDEBP obtained in the presence of Pd(II) catalysts or for t-PDEBP.

ACKNOWLEDGEMENTS

Financial contributions from MURST and CNR (Progetto Finalizzato Chimica Fine II), Italy, are gratefully acknowledged.

REFERENCES

1 Wegner, G. *Z. Naturforsch.* 1969, **24B**, 824

2 Bassler, H., Sixe, H. and Enkelmann, V. in 'Advances in Polymer Science' (ed. H. J. Canton), vol. 63, Springer-Verlag, Berlin, 1984

3 Sandman, D. J. In 'Crystallographically Ordered Polymers', ACS Symposium Series no. 337, American Chemical Society, Washington, DC, 1987

4 Gibson, H. W. In 'Handbook of Conducting Polymers' (ed. T. A. Skotheim), Dekker, New York, 1986, vol. 1, p. 405

5 Bloor, D. and Chance, R. R. (eds) 'Polyacetylenes: Synthesis, Structure and Electronic Properties', Nijhoff, Dordrecht, 1985

6 Dormann, E., Gruner-Bauer, P. and Strohriegl, P. *Makromol. Chem., Macromol. Symp.* 1989, **26**, 141

7 Vinogradov, G. A., Guy, M., Gromov, L. A. and El'yashevitch, M. M. *Makromol. Chem., Macromol. Symp.* 1989, **26**, 165

8 Poole, N. J., Day, R. Y., Smith, B. J. E., Batchelder, D. N. and Bloor, D. *Makromol. Chem.* 1989, **190**, 2909

9 Russo, P. J. and Labes, M. M. *J. Chem. Soc., Chem. Commun.* 1982, 53

10 Colthup, E. C. and Meriwether, L. S. *J. Org. Chem.* 1961, **26**, 5169

11 Stille, J. K. and Frey, D. A. *J. Am. Chem. Soc.* 1961, **83**, 1697

12 Hubert, A. J. and Dale, J. *J. Chem. Soc.* 1965, 3160

13 Gibson, H. W., Bailey, F. C., Epstein, A. J., Rommelmann, H., Kaplan, S., Harbour, J., Yang, X. Q., Tanner, D. B. and Pochan, J. M. *J. Am. Chem. Soc.* 1983, **105**, 4417

14 Kotlyarevskii, I. L., Fisher, L. B., Dulov, A. A. and Slinkin, A. A. *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk* 1960, (5), 950

15 Tani, M., Toda, F. and Matsumiya, K. *Bull. Chem. Soc. Japan* 1963, **36**, 391

16 Kotlyarevskii, I. L., Shvartsberg, M. S., Vasilevskii, S. F. and Andrievskii, V. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1966, (2), 302

17 Shvartsberg, M. S., Kotlyarevskii, I. I., Andrievskii, V. N. and Vasilevskii, S. F. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1966, (3), 527

18 Shishmakova, T. G., Bardamova, M. I. and Kotlyarevskii, I. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1966, (2), 360

19 Kotlyarevskii, I. L., Shergina, S. I. and Zanina, A. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1966, (2), 358

20 Grovu-Ivanoi, M., Bulacovschi, V. and Simionescu, C. I. *Makromol. Chem.* 1985, **186**, 2247

21 Sanechika, K., Yamamoto, Y. and Yamamoto, A. *Bull. Chem. Soc. Japan* 1984, **57**, 752

22 Ortaggi, G., Sleiter, G., D'Ilario, L., Pirozzi, A., Bolasco, A. and Chimenti, F. *Gazz. Chim. Ital.* 1989, **119**, 395

23 Tomassetti, M., Campanella, L., Morgia, C. and Ortaggi, G. *Thermochim. Acta* 1989, **141**, 27

24 Tomassetti, M., Campanella, L. and Mazzei, F. *Thermochim. Acta* 1989, **141**, 41

25 Scofield, J. H. *J. Electron Spectrosc. Relat. Phenom.* 1976, **8**, 129

26 Takahashi, S., Kuroyama, Y., Sonogashira, K. and Hagihara, N. *Synthesis* 1980, 327

27 Furlani, A., Russo, M. V., Camus, A. and Marsich, N. Unpublished results

28 Hartley, F. R. *Organomet. Chem. Rev. A* 1979, **6**, 119

29 Russo, M. V. and Furlani, A. *J. Organomet. Chem.* 1979, **165**, 101

30 Gardella, J. A. Jr, Chin, R. L., Ferguson, S. A. and Farrow, M. M. *J. Electron Spectrosc. Relat. Phenom.* 1984, **34**, 97

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

32 Gustafsson, G., Lundström, I., Liedberg, B., Wu, C. R., Inganäs, O. and Wennerström, O. *Synth. Met.* 1989, **31**, 163

33 Inoue, M. B., Nebesny, K. W., Fernando, Q., Castillo-Ortega, M. M. and Inoue, M. *Synth. Met.* 1990, **38**, 205

34 Bashenko, O. A., Tyzykhov, M. A., Nefedov, V. I., Polzonetti, G., Russo, M. V. and Furlani, A. *J. Electron Spectrosc. Relat. Phenom.* 1991, **56**, 203