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The mechanism of AlN deposition from Me_3Al/RNH_2 mixtures is not known. The greatly lowered growth temperatures (400–600 °C) compared with those reported for the Me_3Al/NH_3 combination (typically >1000 °C) may be due to the presence of a bulky and sterically hindered alkyl (R) group in RNH_2 which lowers the thermal stability of the nitrogen source. It is well established[21] that *tert*-butyl PH_2 and *tert*-butyl AsH_2 pyrolyze at significantly lower temperatures than the parent trihydrides PH_3 and AsH_3. Furthermore, the lower efficiency of *i*-$PrNH_2$ compared with *t*-$BuNH_2$ may simply reflect the relative thermal stabilities of the alkylamines.

Alternatively, it is possible that a complex mechanism is in operation, which involves the formation of gas-phase adducts between Me_3Al and RNH_2 (R = *t*-butyl, *i*-propyl). Such adducts are known[22] to readily form elimination products of the type $[Me_2AlNHR]_2$ and therefore such species may be expected to form in the gas phase upstream from the susceptor. Subsequent pyrolysis of these 'directly bonded' species at or near the substrate may then lead to the β-hydride elimination of the *t*-butyl or *i*-propyl groups. This may then result in the formation of strong intramolecular [Al–N] bonds[16] and facilitate the growth of stoichiometric AlN at low temperature. Support for this mechanism is provided by the formation of a volatile liquid at the reactor inlet, if this is not heated. The lack of dependence of carbon contamination on V/III ratio may also indicate the existence of an active intermediate precursor of fixed Al–N stoichiometry such as $[Me_2AlNHR]_2$.

In conclusion, AlN films, suitable for magnetooptic applications, have been deposited successfully by atmospheric-pressure MOCVD using Me_3Al in combination with the primary alkylamines *t*-$BuNH_2$ and *i*-$PrNH_2$. High growth rates were achieved at moderate substrate temperatures (400–600 °C). The purity of the AlN films was variable, with residual oxygen and with carbon levels which depended on the nature of the alkylamine. A mechanism involving the formation of gas-phase species containing a direct [Al–N] bond has been proposed.

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Electrochemistry of Polydialkylcyclopentadithiophenes—Modulation of π Dimerization by Interchain Spacing Groups**

By *Gianni Zotti*,* *Anna Berlin, Giorgio Pagani, Gilberto Schiavon*, and *Sandro Zecchin*

While polyconjugated conducting polymers in general display a single oxidation cycle, polythiophenes display a twin process with a potential separation of 0.2–0.3 V. Attempts to explain this behavior were first made by Garnier et al.[1] and then in more detail by Heinze et al.,[2] Kankare and co-workers,[3] Diaz and co-workers,[4] and ourselves.[5]

Recently, on the basis of cyclic voltammetry and ESR experiments on end-capped oligothiophenes in the solid state, we attributed the splitting to stabilization of the intermediate polaronic form by π dimerization.[6] Since π dimerization may be in principle removed by a substantial increase of the interchain distance of the polymer strands, we have studied the polymers obtained from anodic coupling of 4,4-di-*n*-alkylcyclopentadithiophene ($(C_n)_2$CPDT, $n = 1$, 3, 4, 6, 8 and 16, see Scheme 1) in which substituents of various lengths are disposed in a symmetrical fashion above and below the coplanar polythiophene ribbon.[7]

This paper reports on a cyclovoltammetric (CV), in situ ESR and UV–vis spectroelectrochemical investigation of these polymers in order to confirm the existence of π dimerization in polythiophene and perhaps to remove or suppress

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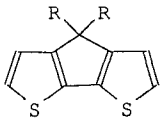

R = H; CPDT
R = CH_3; $(C_1)_2$CPDT
R = n-C_3H_7; $(C_3)_2$CPDT
R = n-C_4H_9; $(C_4)_2$CPDT
R = n-C_6H_{13}; $(C_6)_2$CPDT
R = n-C_8H_{17}; $(C_8)_2$CPDT
R = n-$C_{16}H_{33}$; $(C_{16})_2$CPDT

Scheme 1.

it. The unsubstituted polymer poly(cyclopentadithiophene), polyCPDT, the object of previous electrochemical[8] and spectroelectrochemical[9] investigations, has also been considered for comparison.

While the cyclic voltammogram of polyCPDT displays the twin oxidative redox response commonly found in polythiophenes, poly($(C_n)_2$CPDT) films are characterized by a single well-defined redox response (Fig. 1). The length of the spacing alkyl group is closely reflected in the redox potential E^0 (Table 1), which increases steadily with the number of carbon atoms n in the alkyl chain. This result may be explained by a decreased Coulombic interaction between the polycationic chain and the anion as the distance between the chains becomes larger.

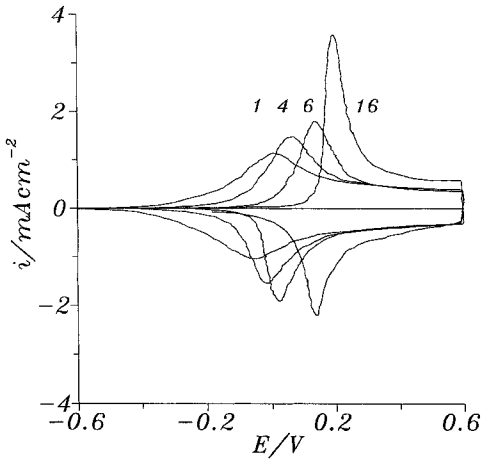

Fig. 1. Cyclic voltammogram for poly($(C_n)_2$CPDT) (n = 1, 4, 6, 16) in CH_3CN 0.1 M TEAP. Scan rate: 0.1 V/s. Reversible charge: 5 mC/cm^2.

A second effect of the interchain spacing groups, which we will take into closer consideration, concerns the peak width of the CV response, which decreases progressively along the series (Fig. 1 and Table 1), approaching a value of 0.1 V . As theoretically expected and recently shown for a series of oligothiophenes in solution,[4, 10] polythiophene oxidation occurs in two consecutive reversible one-electron steps to the radical cation (polaron) and dication (bipolaron) with a potential difference ΔE^0, which decreases as the conjugation length of the polymer chain increases. In our polymer films the two one-electron CV peaks merge into one with a width that is determined by ΔE^0. We have evaluated the ΔE^0 values from the peak width[9] and give them in Table 1. Since the polymer chains contain 20–80 thiophene rings,[7] the expected ΔE^0 values, extrapolated from the linear relationship of ΔE^0 and the inverse chain length using data from the literature,[4] fall in the range 0.035–0.07 V. This figure is comparable with the measured ΔE^0 values for $n \geq 4$ but considerably lower than those for the first members of the series, indicating that in such cases polarons are stabilized in the solid state. Stabilization of radical cations by π dimerization has been recently reported for oligothiophenes in solution[11] and in the solid state.[6] If we attribute to this effect the excess potential difference, neglecting possible adsorptive interactions,[12] it appears that π dimerization operates when the spacing group is absent or small and decreases progressively as the size of the spacing group is increased. For the longest chains ($n \geq 6$) the CV width (ca. 0.1 V) is close to the theoretical value of 0.09 V for two sequential, isoenergetic, one-electron transfers with a statistical separation of 0.036 V,[13] so we expect that in this case π dimerization has been removed. This conclusion is confirmed by ESR experiments.

Table 1. Redox potentials E^0, CV peak width W, potential separation ΔE^0 and spin/electron values at maximum ESR signal s/e for poly($(C_n)_2$CPDT).

n	E^0 [a] [V]	W [b] [V]	ΔE^0 [V]	s/e
0	0.05/0.37		0.31	0.04
1	−0.05	0.35	0.26	0.32
3	0.0	0.24	0.15	0.62
4	0.025	0.17	0.09	0.65
6	0.07	0.11	0.05	0.68
8	0.125	0.10	0.045	0.7
16	0.17	0.10	0.045	0.7

[a] Average of oxidation and reduction peak potentials ($E^0 = (E_{pa} + E_{pc})/2$). [b] Width at half height for films with reversible charge 1–10 mC/cm^2 measured at 0.1 V/s.

Upon oxidation a strong ESR signal is displayed by the polymer films at $g = 2.0025$ with a width of ca. 1.2 G. It increases to a maximum and then decreases to zero following the CV profile (Fig. 2). For the ranges of film thickness and scan rate used, the response is independent of the scan rate, which assures operation under equilibrium conditions. The number of spins per injected electron s/e, measured at the maximum ESR signal, increases as n is increased (Table 1), attaining a limiting value for $n \geq 6$. Thus we may state that π dimerization is virtually absent when $n \geq 6$, confirming the evidence provided by CV. In any case, also at the limit of absence of π dimerization the s/e value (0.7) is less than unity, which is due to the small separation (0.045 V) of the redox potentials. An analogous value has been obtained for polypyrrole,[14] in which π dimerization is absent.

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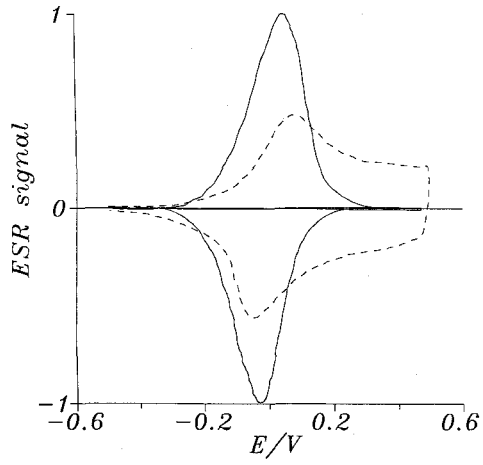

Fig. 2. ESR intensity versus potential for poly($(C_3)_2$CPDT) in CH_3CN 0.1 M TEAP. Scan rate: 0.05 V/s. Reversible charge: 4 mC/cm^2. Dashed line: cyclic voltammogram for comparison.

In the absence of π dimerization, polarons, which could not be clearly detected spectroscopically in polythiophene,[15] would be well evidenced. In situ spectroelectrochemistry (Fig. 3) shows the evolution of the spectrum of poly($(C_8)_2$CPDT) from the neutral state to the fully oxidized state. Upon oxidation a well-resolved band at ca. 1070 nm

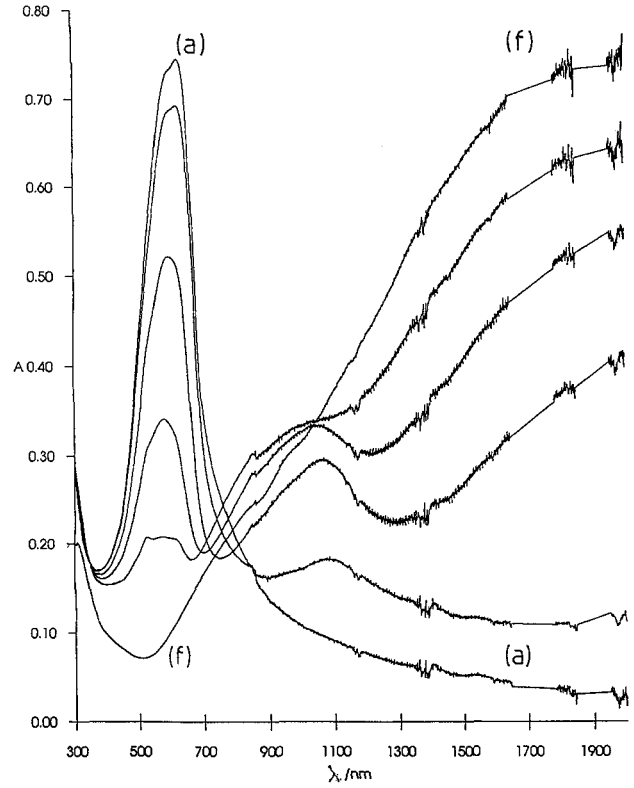

Fig. 3. Spectroelectrochemistry for poly($(C_8)_2$CPDT) in CH_3CN 0.1 M TEAP by charge steps from neutral ($E = -0.2$ V, a) to oxidized ($E = 0.6$ V, f). Percentage charge: a) 0, b) 8, c) 34, d) 60, e) 80, and f) 100%.

develops, attains a maximum at the redox potential and then decreases, merging into the slope of the bipolaronic absorption. In agreement with expectations, progressive oxidation produces a blue shift of the maximum absorption.

Coplanarity of the thiophene rings in the monomers, imposed by the bridging methylene group, and symmetrical disubstitution produces long-range conjugated polymer chains with a regular alternation of the substituent moieties. Within this regular framework radical cations (polarons) π-dimerize to an extent which is modulated by the length of the alkyl group. The strong coupling action (ca. 0.3 eV) present in the unsubstituted polymer, close to the value for PT,[5] is thus progressively reduced and then completely removed. In this way the behavior of polythiophene (CV, ESR, and UV–vis spectroelectrochemistry) agrees with that of the other polyconjugated conducting polymers, and in particular the nitrogen analogue, polypyrrole.

Experimental

Polymer films were produced, as previously reported, by anodic coupling in acetonitrile (AN) of 4H-cyclopenta[2,1-b:3,4-b']dithiophene (cyclopentadithiophene, CPDT)[8] and 4,4-di-*n*-alkylcyclopentadithiophenes ($(C_n)_2$CPDT, $n = 1$, 3, 4, 6, 8, and 16).[7]

Experiments were performed at 25 °C under nitrogen in acetonitrile containing the supporting electrolyte tetraethylammonium perchlorate (TEAP) in 0.1 M concentration. The counter electrode was platinum; the reference electrode was silver/0.1 M silver perchlorate in acetonitrile (0.34 V vs SCE). The voltammetric apparatus (AMEL, Italy) included a 551 potentiostat modulated by a 568 programmable function generator and coupled to a 731 digital integrator.

The working electrode was a platinum minidisc electrode (0.003 cm^2) or a platinum wire (0.05 cm^2) for CV and in situ ESR, respectively. For electronic spectroscopy a 0.8 × 2.5 cm indium tin oxide (ITO) sheet was used.

ESR spectra were taken on an X-band ER 100D Bruker spectrometer following the procedure previously described;[5] absolute spin calibration was performed with $VOSO_4 \cdot 5H_2O$ crystals. Electronic spectra were taken with a Perkin–Elmer Lambda 9 spectrometer.

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