Mixed-valence Perchlorotriphenylmethyl Radical Ion Polymers. A Ten Orders of Magnitude Increase in Conductivity

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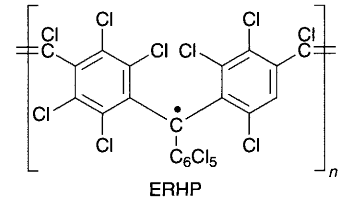
The synthesis and isolation of the first mixed-valence perchloropolymer with perchlorotriphenylmethyl radical and anion units, and vinylene and acetylene bridges has been performed; this new type of material shows promising conducting properties.

The quest for the design of stable, soluble new organic conductors is a subject of increasing interest.[1] A possible new strategy towards conducting polymers is to place known stable radical and ion units in a polymeric chain. Taking into account that perchlorotriphenylmethyl radicals (PTM) and ions are stable solids,[2] and that the intramolecular electron-transfer phenomenon 'spin–charge exchange' takes place in dimeric ion radicals,[3] a similar delocalization is expected in a polymeric chain formed by such types of repeat units. We report here the isolation of the first example of this new type of material and its conducting properties.

With this purpose, we have already synthesized a *trans* polyacetylene precursor: the poly(perchloro-4,4′-dimethyltriphenylmethyl-α′,α″-diylidene) (ERHP), a highly stable polyradical where the PTM radical units are linked together by vinylene bridges.[4] In this polyradical, containing an average of 28 PTM units, it has been shown that: (i) these units are electronically independent (UV–VIS, steric inhibition of resonance); (ii) it is a paramagnetic material (μ_{eff} = 1.65 μ_B at room temp.) with antiferromagnetic interactions at low temperatures; and (iii) it has no electrical conductivity ($< 10^{-12}$ S cm^{-1}).[4] With these results in mind, and ruling out spin-conductivity due to 'spin–spin exchange', the synthesis of mixed-valence polymers, starting from this polyradical, was attempted by a similar two-step route to that already described for a dimeric anion radical:[3,5] (i) the isolation of the polycarbanion using chemical reductors such as potassium[5] or tetrabutylammonium hydroxide (TBAOH),[3] which are known to give stable PTM carbanions with high yields; and (ii) the mixture of equimolecular amounts of the starting polyradical and the polycarbanion in solution.

The reaction of polyradical ERHP with potassium(18-crown-6) in anhydrous THF was monitored by UV–VIS spectroscopy. The vinylenic polycarbanion formed shows a spectrum with a broad band at 525 nm and ε/n = 31500 as expected for PTM carbanions without electronic π–π interactions.[3,4] However, when the solution is treated with ethyl ether in order to isolate the polyanion, the precipitate formed showed an elemental analysis and IR, UV–VIS and ESR spectra which do not agree with those expected for the vinylenic polycarbanion. Its UV–VIS spectrum [Fig. 1(*a*)] displays two additional high intensity bands at 390 (PTM radicals; also confirmed by ESR) and 765 nm (dimeric acetylene PTM radical anion),[5] suggesting that in the precipitation process (under argon, anhydrous medium and without potassium metal) a self-reductive dechlorination of the dichlorovinylenic polycarbanion takes place, giving rise to a mixed-valence polymer. In order to confirm this assertion experimentally, the gradual oxidation with I_2 in THF of this mixed-valence polyradical polyanionic solid was monitored by UV–VIS spectroscopy. Surprisingly, the reaction takes place in two definite steps: (i) [Fig. 1(*a*)–(*c*)] the oxidation of vinylene PTM carbanions (decrease of the band at 525 nm) to vinylene PTM radicals (increase of the band at 390 nm, *ca.* 25%); and (ii) [Fig. 1(*d*)–(*f*)] the oxidation of acetylene radical anion units[5] (decrease of the band at 765 nm, *ca.* 25%) to acetylene PTM radicals (increase of the bands at 390, 445 and 664 nm, *ca.* 25%). The isolation of the oxidation product yields a stable green polyradical with a UV–VIS spectrum [Fig. 1(*f*)] that differs from the initial red ERHP polyradical in two additional absorptions (445, 664 nm) owing to the existence of acetylene PTM radical units (*ca.* 25%).[4] Chlorination of this green polyradical with Cl_2–I_2 affords an 87% of a red polyradical, identical to the initial vinylenic ERHP with high radical purity (95%), identified by elemental analyses, IR, ESR and UV–VIS spectra.[4] Also, the reaction of polyradical ERHP with TBAOH (large amounts) in THF and subsequent precipitation with hexane–water[3] does not give the corresponding vinylenic polycarbanion, but the above mixed-valence polymer (UV–VIS).

Taking into account: (i) the results of the elemental analyses (C, H, Cl); (ii) the fact that the reductive dechlorination of the dichlorovinylene group is a two-electron-transfer reaction;[6] (iii) the fact that the UV–VIS spectrum of the mixed-valence



ERHP

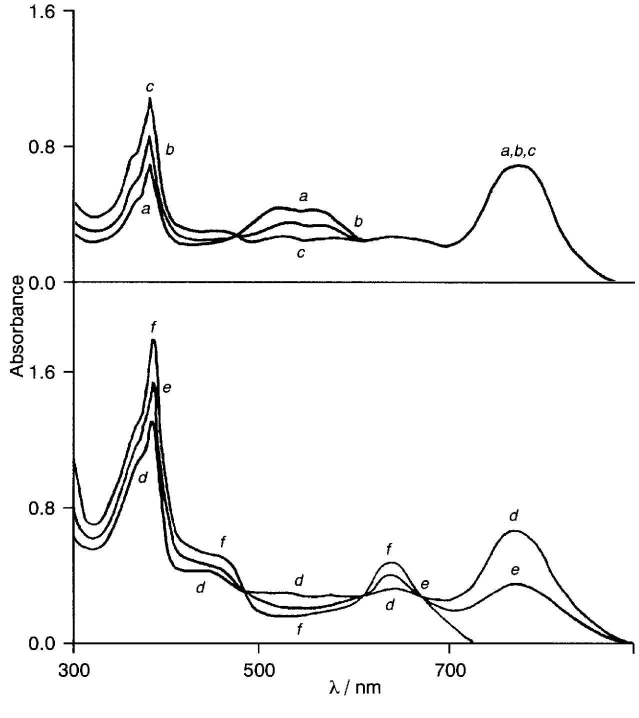


Fig. 1 UV–VIS monitoring of the oxidation of the mixed-valence polymer with iodine. First step [top, (*a*)–(*c*)], formation of vinylene PTM radicals; second step [bottom, (*d*)–(*f*)], formation of acetylene PTM radicals.

polymer agrees with being a mixture of the UV–VIS spectra of vinylene[3] and acetylene[5] PTM radical anions; and (iv) the results of the above-mentioned oxidation with I_2, we propose the following alternate structure:

$$-PTM^{\cdot}-C{\equiv}C-PTM^{-}-CCl{=}CCl-PTM^{\cdot}-CCl{=}CCl-PTM^{-}-CCl{=}CCl-$$

This interesting structure is formed by acetylene PTM anion radical units (Class III, resonance)[5] and vinylene PTM anion radical units (Class II, spin–charge exchange),[2,3] both being dimeric groups with different chemical and physical properties.

One possible explanation for the high reactivity of dichlorovinylene PTM polycarbanion when compared with the overwhelming majority of stable PTM carbanions[6] is the intrinsic reactivity of dichlorovinylene group as electronic acceptor[7] and the high steric strain in the polymeric chain (the UV–VIS spectrum of the vinylenic polycarbanion shows steric inhibition of resonance) which does not allow relaxation of the coulombic forces by changes in the very rigid geometry, or by resonance. In fact, the electron-transfer reactions from the PTM carbanions to the vicinal dichlorovinylene groups produce acetylene PTM anion radicals with an estimated resonance stabilization energy of *ca.* 18 kcal mol^{-1},[5] lower steric strain and the alternation of spin-charges in the polymeric chain. As a result, the lowering of steric and coulombic forces are thermodynamically favoured as is evidenced in the solid state, where stabilization by solvation is not operative.

Conductivity measurements of the mixed valence polymer in compressed pellets show a value of 2.0×10^{-2} S cm^{-1}, while polyradical ERHP has a value of $<10^{-12}$ S cm^{-1}; a similar increase in conductivity has been described in polyacetylene (10^{-5} to 10^{5} S cm^{-1}). Accordingly, a long absorption tail observed in the IR spectrum (4000–1700 cm^{-1}) is attributed to charge transfer owing to 'intermolecular spin–charge exchange' in the solid.[8] The ESR spectrum of the solid sample shows a single symmetric broad line (g = 2.0031) with a ΔH_{pp} of 6.1 G that becomes narrower (2.6 G) in isotropic solution at room temperature; the similarity of this spectrum with that of poly[perchloro-(4,4′-dimethyltriphenylmethyl)-α,α′-diylidyne] ARHP[4] confirms that they are structurally related (presence of triple bonds). The magnetic data did not show any significant anomalous behaviour.

Consequently, it has been shown for the first time that mixed-valence perchlorotriphenylmethyl polymers have good semiconducting properties. In order to improve both conductivity and stability it seems promising to synthesize this new type of polymer containing regular structures without electroactive bridges.

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