

Proton abstraction as a route to electrically conductive polymers

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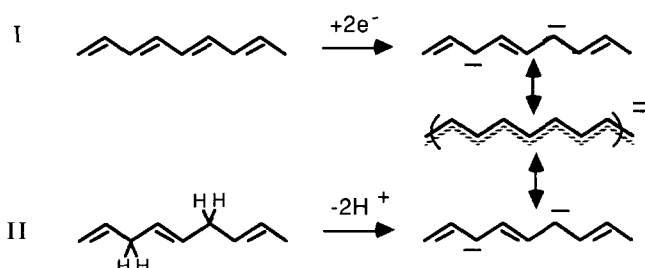
Proton abstraction with a strong base from relatively acidic doubly allylic and/or benzylic methylene moieties spaced along an otherwise all-conjugated polymer chain has been demonstrated as an alternative route to electrically conductive polymers. Poly(*p*-phenylene pentadienylene) and its model compound 1,5-diphenylpentadiene, have been prepared via a Wittig reaction sequence. Proton abstraction from the methylene moiety of the model compound to form the delocalized carbanion has been achieved through reaction with *n*-BuLi and has been confirmed by reaction with methyl iodide. Proton abstraction from poly(*p*-phenylene pentadienylene) oligomers has been achieved by treatment with *n*-BuLi to yield a blue-black solid. Preliminary results indicate a conductivity of 10^{-1} – 10^0 S cm $^{-1}$ for a pressed pellet of the blue-black solid.

(Keywords: conductive polymer; proton abstraction; doping)

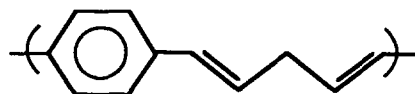
Interest in conductive polymers has been intense ever since the original demonstration of polyacetylene's unique electrical behaviour upon treatment with electron donors or acceptors¹. Since then many other all-conjugated polymers have been shown to be capable of forming electrically conductive materials on doping (e.g. poly(*p*-phenylene), polypyrrole, poly(phenylene sulphide)²). Although these have demonstrated the real possibility of electrically conductive organic polymers, they generally suffer from many problems and handicaps that preclude their use as precursors to conductive materials. These problems include their poor environmental stability, intractability, poor mechanical properties, and/or the necessity of using toxic dopants. With such formidable obstacles, it is obvious that an alternative route to electrically conductive polymers would be of considerable interest. This work presents such a route developed from the currently accepted model that attributes polymeric conductivity to charged delocalized centres along the polymer backbone³. From this, a novel polymer system was designed, synthesized and shown to be conductive upon simple chemical treatment.

Conventional *n*-doped conducting polymers, prepared by the reduction of fully conjugated polymers, are proposed to have the electronic structure of carbanions fully delocalized along the conjugated polymer backbone, I³. An alternative route to an identical delocalized carbanion structure is through proton abstraction from methylene moieties spaced along an otherwise all-conjugated polymer backbone, II.

The relative acidity of the doubly allylic methylene moieties as seen in II makes proton abstraction by base plausible, as has been demonstrated for many low molecular weight compounds^{4,5}. Although proton abstraction has been considered in discussions of conducting polymers, it has not been proposed as a primary doping mechanism⁶.

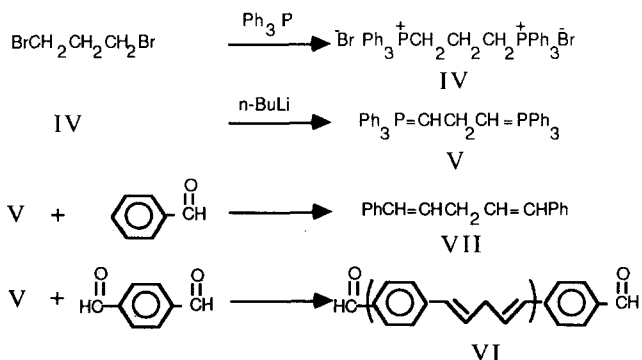


To demonstrate proton abstraction as a primary doping mechanism, a suitable polymer precursor needed to be identified and prepared. Many polymer structures including doubly allylic and/or benzylic methylene moieties can be imagined. One example is poly(*p*-phenylene pentadienylene), III.



III

This polymer and a model compound, 1,5-diphenylpentadiene, have been prepared via a Wittig reaction scheme, as shown below.



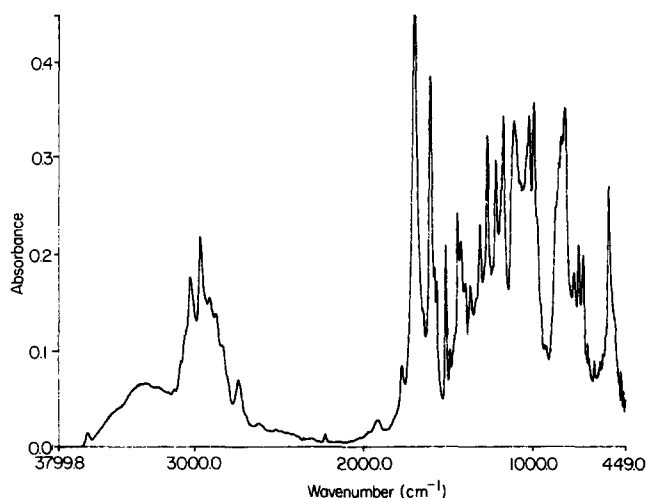


Figure 1 Diffuse reflectance infra-red spectrum of poly(*p*-phenylene pentadienylene)

Oligomers, VI, have been prepared by varying the molar ratio of terephthalaldehyde and bisylid V, always using excess aldehyde. The ^1H n.m.r. spectrum shows the expected absorptions for the aldehyde end groups (9.9 ppm; intensity dependent on molecular weight), aromatic and olefinic protons (7.8–5.8 ppm) and the methylene protons (3.3 ppm). Intensity ratio of the aldehydic to aromatic/olefinic absorptions yields a degree of polymerization of 7.3, in fair agreement with the g.p.c. polystyrene-equivalent number-average molecular weight of 1700 ($DP = 12$). Infra-red absorptions (Figure 1) are consistent with the proposed structure and are assigned as follows: 3020 cm^{-1} , unsaturated C–H stretch; 1700 cm^{-1} , C=O stretch (aldehyde end groups); 1605 and 1510 cm^{-1} , aromatic ring modes; 995 and 825 cm^{-1} , C–H out-of-plane bend.

Model compound VII was prepared through the reaction of bisylid V with benzaldehyde. The product was purified via distillation at 127°C – 132°C at 0.5 mm Hg (ref. 7: 205 – 211°C at 12 mm Hg) and characterized via ^1H n.m.r. and infra-red spectroscopies. ^1H n.m.r. (60 MHz, ppm, CDCl_3) 7.15 (s, 5H, aromatic), 6.6–5.6 (m, 2H, olefinic) and {3.3(d) and 2.9(t) (methylene, 1H total; 80:20/1.3-pentadiene:1,4-pentadiene)}; FTi.r. (cm^{-1}) 3020 (s), 1500 (s), 995 (s), 780 (s) and 740 (s).

Proton abstraction was first demonstrated with VII, as shown below, VIII. Anion formation was evident through the intense blue–black solution formed on addition of *n*-

BuLi, the rapid quenching of the colour on addition of CH_3I , and characterization of the methylated product, VIII, and other isomers by proton n.m.r. ^1H n.m.r. (60 MHz, ppm, CDCl_3) 7.15 (s, 10H, aromatic), 6.7–5.7 (m, 4H, olefinic), 3.25 (m, 1H, methine) and {1.3(d), 1.25(d) and 1.15(d) (methyl, 3H total)}).

Preliminary doping of oligomers of structure VI has been achieved. Addition of *n*-BuLi to a tetrahydrofuran (THF) solution of oligomers yields an intensely coloured blue–black precipitate, indicative of anion formation. The solid was washed twice with THF, then dried. Preliminary results indicate a conductivity of 10^{-1} – 10^0 S cm^{-1} for a pressed pellet of the blue–black material (conductivity was measured under pressure in a sealed cell by using two stainless-steel pressure contacts and a Data Precision 2440 multimeter). An estimate of the efficiency of proton abstraction doping was obtained by quenching the doped material and exhaustive extraction with methanol. Lithium ion concentration of the methanol solution as determined by atomic absorption spectroscopy indicated a minimum lithium content of one Li^+ per 1.4 repeat units. It is also noted that upon treatment of a solution of oligomers with sodium naphthalide radical anion, a typical electronic reducing agent, no change is observed in the oligomer solution with the exception that it takes on the dark green colour of the sodium naphthalide radical anion. The failure of a strong electronic reducing agent (sodium naphthalide) to dope poly(*p*-phenylene pentadienylene) oligomers along with the typical strong base chemistry displayed by the reaction of VII with *n*-BuLi suggests that proton abstraction is the predominate doping mechanism for the oligomer/*n*-BuLi system.

Proton abstraction doping as an alternative route to conductive polymeric delocalized carbanions has the advantage of starting from a polymeric precursor that is not fully conjugated. Through break-up of the conjugated sequence lengths, polymeric precursors of this type are expected to be more stable to oxidation and to be more physically manageable through enhanced solubility and processability.

ACKNOWLEDGEMENT

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