Communications

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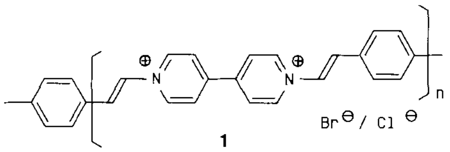
Poly-[*N*,*N*-(1,4-divinylbenzene-β,β'-diyl)-4,4'-bipyridinium dibromide], a Novel Conducting Viologen Polymer**

By *Andreas Merz** and *Stefan Reitmeier*

Dedicated to Professor Gottfried Märkl
on the occasion of his 60th birthday

The title compound **1** is a new, easily accessible π-conjugated viologen polymer. Properties of particular interest are its conductivity of 1×10^{-3} S cm^{-1} and electroactivity in the potential region from −0.1 to −0.6 V vs. Ag/AgCl.



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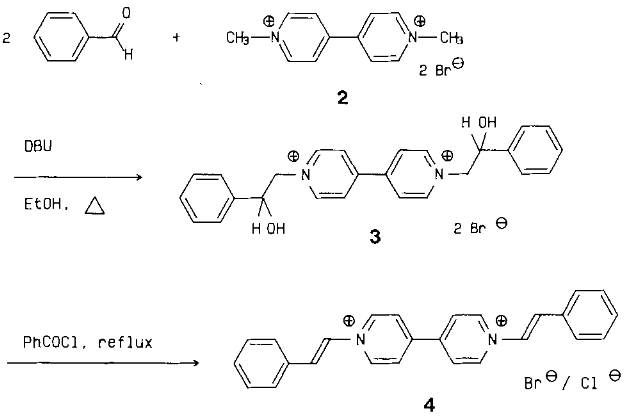
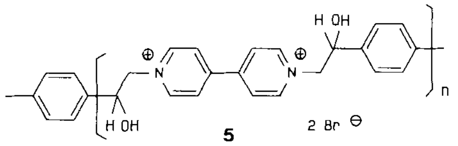
The electrical conductivity of π-conjugated electron rich organic polymers like polypyrrole, polythiophene, and polyaniline is increased by chemical or electrochemical oxidation (p-doping with positive charge carriers).[1] The doping process occurs simultaneously with polymer film formation at the electrode surface during anodic oxidation. On discharging at negative potentials in an electrochemical cell the polymer films become insulating. Polyphenylene and polyacetylene are also electroactive at very negative potentials.[2] The reduction process corresponds to n-doping with negative charge carriers. It was assumed that suitable π-conjugated polymeric viologen structures should be reducible at moderately negative potentials and possibly show conductivity in this potential region.

Methyl viologen **2** displays two reversible redox transitions at −0.57 and −0.92 V.[3] Compound **2** and its homologues have frequently been used as redox catalysts[4] and as electron relays in photocatalyzed water cleavage.[5] Polymeric viologens are also known, with the viologen moiety either as a pendant group on the polymer chain,[6] or as an interconnecting member of the chain.[7]

The orange styryl viologen **4** was prepared as a model monomer in a two step synthesis, following a procedure of *Kröhnke* for the preparation of *N*-alkenyl pyridinium salts,[8] starting from methyl viologen and benzaldehyde and proceeding via the bis-hydrated salt **3** (Scheme 1).[9] The 250 MHz ^{1}H NMR shows that the *E*/*Z* ratio of the styryl units of **4** is 3.6:1. The extended π-system of **4** as compared with **2** is demonstrated by a positive shift of the viologen redox signals and the presence of a third reversible couple which is not likely to be due to the *E*/*Z* isomers.[10]



The same synthetic method is readily applied to the preparation of **1**.[11] Reaction of methyl viologen with 1,4-benzenedialdehyde (1:1) in 90% aqueous ethanol, in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) for 3–4 d at 70 °C gives the polyhydroxy salt **5** as a tan solid in 60% yield. After drying, this is converted to **1** by dehydration in neat benzoylchloride for 10 h at 100 °C.



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Polymer **1** is obtained as an amorphous black powder. It is paramagnetic, giving a single unresolved ESR signal with $g = 2.009$, a peak to peak width of 5.9 G and a spin density of 5×10^{-17} spins per gram. Elemental analysis shows that the bromide anion has been partially exchanged for chloride which stems from the dehydrating agent. The halogen content is 30% less than calculated for **1** although the C:H:N ratio is correct. The same effect is observed for the hydroxypolymer salt **5**. The reason for the deviation from the stoichiometric values is not clear at this time, although it may result from the terminal groups or from the irreversible side reaction of some viologen groups. The IR spectrum suggests the presence of water (see[8]) and possibly the benzoate anion. The presence of conjugated viologen structural elements has been confirmed by cyclic voltammetry of 5% of **1** in a

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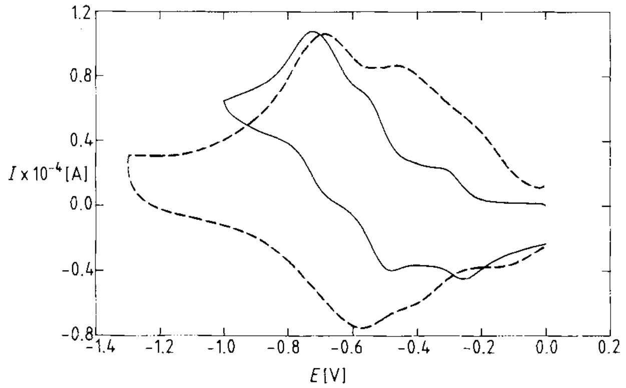

Fig. 1. Cyclovoltammograms of **1** and **4**. (---): Voltammogram of **1** embedded in a carbon paste electrode [12] in DMSO/0.1 M Bu_4NClO_4, scan rate 1 mV s^{-1}, E_p(red) = −0.20, −0.46, −0.69 V; E_p(ox) = −0.15, −0.41, −0.58 V. (— —): Solution cyclic voltammogram of **4** in DMSO/0.1 M Bu_4NClO_4 on a 0.07 cm^2 Pt disk; scan rate 0.1 V s^{-1}, current scale in this case should be changed to 10^{-5}. Potentials are recorded vs. Ag/AgCl [3]. E_p(red) = −0.31, −0.55, −0.71 V; E_p(ox) = −0.26, −0.48, −0.68 V.

carbon paste electrode[12] (Fig. 1). The voltammogram is very similar to that of **4**. The further positive shift indicates more extended conjugation. The area under the slow sweep voltammogram in Figure 1 corresponds to 1.4 F mol^{-1} for both reduction and oxidation.

Polymer **1** is easily pressed into pellets which have an electrical conductivity[13] of $(1.3 \pm 0.2) \times 10^{-3}$ S cm^1. Neither the ESR spectrum nor the conductivity change on storage in air for two months. Likewise, **1** is stable in water and in many organic solvents. Exposure of the polymer to iodine vapors increases its conductivity by a factor of 2–3. Gaseous SO_2 has no effect. Doping experiments in solvent suspensions with I_2 and $FeCl_3$ for the oxidative process, or with $Na_2S_2O_4$ for the reductive process resulted in almost complete loss of conductivity. Thus, it appears that the necessary conditions for conductivity are produced during the dehydration process without the need for additional doping.

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[3] The potentials reported were measured vs an AgCl coated silver wire in dimethyl sulfoxide (DMSO); the zero potential on this scale is 339 mV negative of the ferrocene signal.

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[9] ^1H NMR spectrum of **3** (in CD_3OD): $\delta = 4.54$ (2H; OH), 4.82 (2H; CH_2), 5.05 (2H; CH_2), 5.27 (1H). ABX system with $J_{AB} = 15.8$ Hz, $J_{ax} = 8.0$, $J_{BX} = 3.1$; C*H*OH), 7.32–7.51 (10H, m; C_6H_5), 8.67 (4H), 9.18 (4H, AA'BB' system with $J_{AB} = 6.2$ Hz). Voltammetric data of **3**: E_p(red) = − 0.57, −0.94 V; E_p(ox) = −0.49, −0.87 V.—^1H NMR spectrum of **4** in $[D_6]$DMSO: $\delta = 7.53$–7.66 (6H, m; *m*-, *p*-C_6H_5), 7.72–7.78 (4H, m; *o*-C_6H_5), 7.94 (0.44H), 8.43 (0.44H, AB system with $J_{AB} = 14.2$ Hz), 8.79 (0.88H), 9.53 (0.88H, AA'BB' system with $J_{AB} = 6.6$ Hz), 8.05 (1.56H), 8.51 (1.56H, AB system with $J_{AB} = 14.5$ Hz), 9.02 (3.12H), 9.70 (3.12H, AA'BB' system with $J_{AB} = 6.6$ Hz). UV spectrum of **4**: $\lambda_{max} = 362$ nm ($\varepsilon = 2.21 \times 10^4$).

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[11] C, H, N, Hal. analysis found (calculated): **1** $(C_{20}H_{16}Br_{1.66}Cl_{0.33}N_2)_n$, (428.7) × n: C 56.1(56.0), H 4.2(3.7), Br 20.5(30.9), Cl 1.8(2.7), N 5.5(6.5). **5** $(C_{20}H_{20}Br_2N_2O_2)_n$, (464.7) × n: C 50.2(50.0), H 5.0(4.2), Br 23.5(33.5), N 5.7(5.8).

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Probing Changes in the Structure and Performance of a Lithium Nickel Oxide Catalyst by in situ X-Ray Diffraction During the High-Temperature Oxidative Coupling of Methane[**]

By *Ingrid J. Pickering*, *Peter J. Maddox* and *John M. Thomas*[*]

Heterogeneous catalysts and their precursors are customarily characterized under conditions profoundly different from those that prevail in the actual catalytic reaction. The active solid may possess structural features quite unlike those deduced from measurements conducted at ambient temperatures and pressures. This calls for the increased use of in situ methods for the characterization of heterogeneous

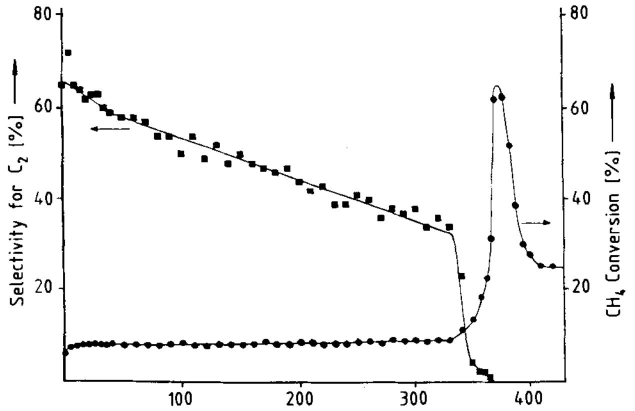

Fig. 1. The changes with time of conversion of methane and selectivity for C_2 hydrocarbons are shown for the duration of the experiment. Percentage conversion of methane is derived as $(100 \times \Sigma n V_{C_n})/V_{CH_4} + \Sigma n V_{C_n}$ and percentage selectivity for ethane and ethene as $(100 \times (2 V_{C_2H_6} + 2 V_{C_2H_4}))/\Sigma n V_{C_n}$ where V_{C_n} is the percentage volume of C_n hydrocarbon product (CO, CO_2, C_2H_4, C_2H_6) in the gas chromatographic analysis. (These values do not take into account any carbon which forms carbonate or other solid phases).

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