Poly(Alkylene Phosphates) as New Dopants of Polyaniline

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Polyaniline, soluble in the protonated state, has been prepared by doping of polyemeraldine with poly(alkylene phosphates).

The solubility of conducting polymers is of crucial importance for their applications. Polymers such as polyacetylene,[1] poly(*p*-phenylene),[2] polypyrrole[3] were insoluble and for this reason practically impossible to process. Elsenbaumer *et al.*[4] demonstrated that polythiophenes substituted in the 3 position of the thiophene ring with an alkyl group are soluble in common organic solvents, such as toluene or chlorinated hydrocarbons. However, poly(3-alkylthiophenes) have one major disadvantage, namely they are soluble in the undoped, *i.e.* nonconducting state and upon doping their solubility drastically decreases.

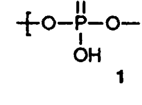
Recently conducting polymers soluble in the conducting state have been prepared *via* protonation of polyaniline with suitable sulfonic acids[5] or phosphoric acid esters.[6–8] However, polyaniline doped with low-molecular mass compounds might deprotonate in alkaline media. This would inevitably lead to a decrease of conductivity. One possible approach developed to overcome this is the use of polymeric-type protonating agents. Macromolecular compounds suitable for the preparation of solution processable conducting polyaniline must possess a sufficient number of acidic sites in the chain capable of protonating polyaniline, and the resulting composite of molecular type, which involves protonated polyaniline and counterions chains of polymeric nature must provide stable solutions.

Poly(alkylene phosphates), PAPs, **1**, look excellent candidates for the preparation of these molecular composites. They are strongly acidic and the number of acidic sites in their chains can be changed by altering the length of alkylene spacer between the phosphoric groups, *i.e.* they can be tailored to prepare conducting composites with different protonation levels.[9,10] Moreover, one can easily modify the chemical structure of the hydrocarbon bridges. Poly(alkylene phosphates) were prepared by polycondensation of dimethyl phosphate with corresponding diols and then oxidised with N_2O_4 to polyphosphates.[9,10] Number average molecular mass, M_n, as determined by osmometry varied from 9000 to 14000.

Polyaniline, PANI, in the oxidation state of polyemeraldine can be conveniently doped with poly(alkylene phosphates) dissolved in EtOH–H_2O (2:3). However, the protonation product is not soluble in the doping medium. For a given ratio of PAP unit to PANI unit the conductivity decreases with the increase of the number of methylene groups in the spacer. In PANI$(PAP)_{0.25}$ the conductivity changes from 1.5×10^{-1} S cm^{-1} for $n = 5$ (where n = number of methylene groups) to 6×10^{-4} S cm^{-1} for $n = 12$ (measured on pressed pellets).

It is known that polyemeraldine base can be dissolved in *N*-methylpyrrolidinone, NMP[11], giving a deep-blue solution with two distinct absorptions in the UV–VIS region: 325 nm ascribed to the π-π^* transition; 635 nm associated with the exciton formation in the quinoid rings.[12]

If the polyemeraldine/NMP solution is mixed with PAP solution in the same solvent, colour changes occur from blue to different shades of green depending on the molar ratio of PAP to PANI. These solutions are stable and no precipitation could be observed even over several months of storing at room temp. Close inspection of UV–VIS spectra of PANI/PAP solutions gives strong evidence for the protonation of PANI with PAPs. In particular, the two previously mentioned transitions, characteristic of the undoped state, diminish their intensities with the increase of PAP/PANI molar ratio and two new transitions (*ca.* 425 nm and 900 nm), typical of the protonated state appear. The existence of the isosbestic points at 460 and 770 nm proves that only two optically different phases coexist (protonated and non-protonated). For PAP with a shorter spacer ($n = 5$) the features characteristic of the undoped state disappear totally whereas for those with a longer spacer ($n = 8$) complete protonation is never achieved. This observation is consistent with the results of conductivity studies.



$$\left[\mathrm{O{-}\overset{\displaystyle O}{\underset{\displaystyle OH}{P}}{-}O{-}(CH_2)_n}\right]_x$$

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Films can be cast from PANI/PAP/NMP solutions. UV–VIS spectra of these films also show the features characteristic of doped polyaniline, *i.e.* the transitions at 320, 436 and 794 nm can be observed. Moreover, the PAP/PANI films are more resistant to deprotonation than the PANI films doped with low-molecular mass compounds. For example, a thin film of polyaniline doped with 1 mol dm^{-3} HCl solution deprotonates almost completely (the peaks at 320 and 636 nm) after its immersion into distilled water for 0.5 h, whereas the PANI/PAP film has features typical of the protonated state (the peaks at 320, 436, 746 nm) even after 20 h of washing with water.

FTIR spectra of polyaniline doped with PAPs have features characteristic of the protonated state, namely: quinoid, N=Q=N, (1584 cm^{-1}) and benzoid, N–B–N (1494 cm^{-1}) ring stretching modes of polyemeraldine are shifted towards lower frequencies, *i.e.* 1566 and 1487 cm^{-1}, respectively; 1134 cm^{-1} band diagnostic of the protonated state appears; all of the most intensive bands of PAPs, *i.e.* 1050, 993, 795 cm^{-1} corresponding to ν(P–O–C) and $\delta(CH_2)$ are present; 1248 cm^{-1} band of ν(P=O) is superimposed with 1230 cm^{-1} of stretch in BBB of polyaniline.

More detailed information concerning the protonation state in solid PANI/PAP can be extracted from XPS measurements. The N1s spectra of PANI$(PAP)_{0.52}$ ($n = 6$) can be deconvoluted into three peaks corresponding to imine, amine and positively charged nitrogens with chemical shifts of 398.3, 399.2 and 401.0 eV respectively.[13] The intensity of imine band decreases upon the increase of PAP/PANI ratio indicating preferential protonation of imine sites. Of course, XPS N1s probes only the protonation of polyemeraldine chain and does not give information about the fraction of POH groups of PAP participating in the protonation. This information can, in turn, be extracted from the P2p spectra. These spectra can be deconvoluted into two doublets assigned to negatively charged phosphates, PO^-, (P2p3 = 132.8 eV) and to unionized phosphates, POH, (P2p3 = 134.5 eV). Unionized phosphates can be observed even for low PAP/PANI molar ratio, *i.e.* in the presence of imine groups of polyaniline. The evolution of N1s and P2p spectra clearly demonstrates that poly(alkylene phosphates) can protonate polyemeraldine, however, the protonation level is strongly influenced by the equilibrium between both polymers. XPS can also give important information concerning the chemical composition of the blend. It shows that P/N ratio (where N corresponds to amino and imino groups of PANI) in the dried film is essentially the same as in the solution used for casting (0.51 and 0.52, respectively). Since XPS is a surface probe this result implies that the dopant is uniformly distributed in the blend. For some samples an additional peak (at 396.9 eV) assigned to NMP nitrogen can be seen. Complete removal of NMP from the system is very difficult (specially for thick samples) and requires extended pumping and heating.

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