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"Pseudo-Protonic Acid Doping" of Polyaniline[†]

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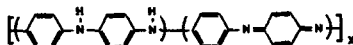
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and

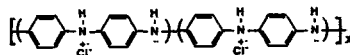
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The emeraldine oxidation state of polyaniline, in its base form

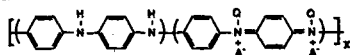


may be doped to the metallic conducting regime by aqueous HCl in a novel protonation reaction to form the corresponding emeraldine hydrochloride salt which exists as the paramagnetic semiquinone radical cation:



We now find that a large new class of N-substituted derivatives of emeraldine may be synthesized by a "pseudo-protonic acid" doping process involving the reaction of emeraldine base with reagents such as Me₂SO₄, Et₂SO₄, C₆H₅CH₂Br, H₂C=CHCH₂Br, Me₃SiCl, C₆H₅C(O)Cl, C₆H₅SO₂Cl, MeC₆H₄SO₂Cl, ClO₂S(C₆H₄)SO₂Cl and o-NO₂(C₆H₄)SCl etc. to yield products which from preliminary studies are believed to have the above semiquinone radical cation structure, i.e. polaronic structure, where Q = Me, Et, C₆H₅CH₂, H₂C=CHCH₂, Me₃Si, C₆H₅C(O), C₆H₅SO₂, Me(C₆H₄)SO₂, O₂S(C₆H₄)SO₂, o-NO₂(C₆H₄)S etc. and A = Cl, Br, MeSO₄ and EtSO₄.

In certain cases involving a variation in experimental conditions it seems possible that the bipolaronic form



of the polymer might be produced. Many of these polymers show significant solubility in several organic solvents and may be prepared as films and/or powders exhibiting conductivities up to ~50 S/cm. This work was supported by NSF Grant No. DMR-85-19059 (M. A.), NASA Grant No. NAG10-0025 (S. K. M.) and a grant from Lockheed Corp. (S. P. E.).

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