POLYANILINE: *PERNIGRANILINE*, AN ISOLABLE INTERMEDIATE IN THE CONVENTIONAL CHEMICAL SYNTHESIS OF *EMERALDINE*

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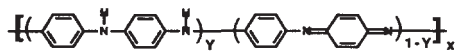
ABSTRACT

The conventional chemical oxidative polymerization of aniline to polyaniline in the *emeraldine oxidation state* using acidic ammonium peroxydisulfate (aniline:peroxydisulfate ~4:1; aq. 1.0N HCl; ~0 °C) was found to proceed via the intermediacy of the fully oxidized *pernigraniline oxidation state* (readily isolable as the base form). The intermediacy of the pernigraniline oxidation state was first detected by using a novel potential profiling technique in which the oxidation potential of the system was continuously monitored as a function of polymerization time.

INTRODUCTION

The base forms of polyaniline are described by a series of polymers having different oxidation states as represented by the general formula [1]



ranging in principle from the completely reduced to the completely oxidized members. The emeraldine oxidation state (y~0.5) which consists principally of alternating reduced and oxidized repeat units [2] has recently aroused considerable interest [1,3,4], since on protonation with aqueous acids such as HCl, its conductivity is increased by ~10 orders of magnitude (compressed pellet, 1-5S/cm [1,3]; stretched-aligned fibers, ~10^2S/cm [4]) to give a polysemiquinone radical cation having a half-filled polaron conduction band [1,4,5,6].

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RESULTS

The emeraldine oxidation state is most commonly synthesized as the insoluble hydrochloride by the oxidative polymerization of aniline in aqueous HCl by $(NH_4)_2S_2O_8$. A series of color changes is observed during the reaction. We were surprized to find that the the precipitate which is first formed when excess aniline is used consists of polyaniline in the pernigraniline oxidation state (y~0) [7] and that this subsequently oxidatively polymerizes excess aniline if present, while at the same time it is itself reduced to the emeraldine oxidation state. The study of these reactions which involve significant changes in oxidation state of both reactants and products was made possible by using a potential profiling technique whereby the changing potential of the system was constantly monitored throughout the course of the reaction [8].

When the synthesis is carried out at ~0°C using excess aniline [1] the initial oxidation potential of the reaction system increases from ~0.40V (vs. SCE) (Fig. 1, point A)

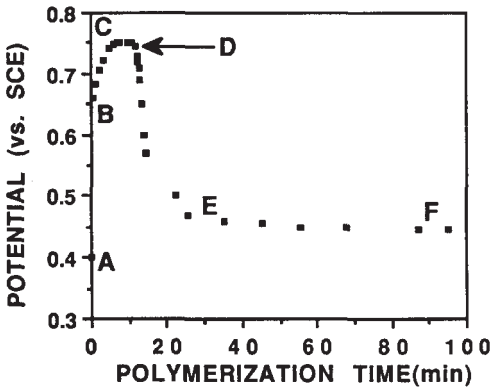

Fig. 1. Potential-time profile of a conventional chemical oxidative polymerization of aniline using ammonium peroxydisulfate in aq. 1.0N HCl (Pt electrode; SCE reference).

to ~0.66V (point B) immediately after adding the $(NH_4)_2S_2O_8$, to ~0.75V (point C), within ~3.5 minutes at which value it stays essentially constant before it begins to fall rapidly after ~10 minutes, reaching ~0.47V at point E, and ~0.44V at point F, values close to that of the emeraldine oxidation state [9]. The temperature increases noticeably after point D is reached. The above times and potentials are, of course, dependent on the temperature at which the reaction is studied. If the reaction mixture at point D is poured into cold (~5°C) aqueous NaOH solution, analytically

pure pernigraniline base powder [10] which has an oxidation state (1-y) = 0.96+0.02 by $TiCl_3$ titration [11] is obtained. Its electronic and infrared spectra are identical to those of pernigraniline base powder synthesized independently using *m*-$Cl(C_6H_4)C(O)OOH/N(C_2H_5)_3$ [7].

At point D, the $(NH_4)_2S_2O_8$ (whose concentration was monitored continuously with time and determined quantitatively by titrimetric estimation [12]) was essentially all consumed. If the reaction mixture was poured into aqueous NH_4OH between points E and F, polyaniline in the emeraldine oxidation state was obtained. When the pure pernigraniline base, isolated at point D was treated with an excess of a mixture of aniline and HCl of the same relative concentration as that employed in the initial polymerization reaction (but with the omission of $(NH_4)_2S_2O_8$), analytically pure emeraldine base was obtained [13].

The above observations are consistent with the following hypothesis: The potential at which aniline undergoes electrochemical oxidation in aqueous acid is ~0.7V (vs. SCE) [9]. The potential of the 0.1M solution of $(NH_4)_2S_2O_8$ in 1.0N aqueous HCl before adding aniline is ~1.05V [14] and that of pernigraniline and emeraldine bases in 1M HCl are ~0.83V [7] and ~0.43V [9] respectively. The $(NH_4)_2S_2O_8$/HCl system is therefore expected to produce, as has now been found experimentally, at least initially, polyaniline in its highest (pernigraniline) oxidation state. The pernigraniline is a sufficiently strong oxidizing agent to oxidatively polymerize any excess aniline to the emeraldine oxidation state, while it is itself reduced also to the emeraldine oxidation state. The emeraldine oxidation state finally obtained as point F is approached is therefore formed in two different ways: (i) by the reduction of the pernigraniline initially formed and (ii) by the oxidative polymerization of aniline by pernigraniline.

During polymerization, a thin film of polyaniline is deposited on the walls of the beaker and on any inert substrate, e.g., microscope slide present in the reaction mixture by *in-situ* adsorption polymerization [8,15]. Substrates were immersed in the acidic aniline solution prior to the addition of the oxidant and were removed at various intervals and quenched in aq.NaOH. At point D, after treatment with aqueous NaOH, the film deposited on a microscope slide was identified by its electronic spectrum as pernigraniline base. Thin, transparent and strongly adhering films of pernigraniline base of increasing thicknesses were obtained upon removing the substrates between points C and D in Fig. 1. The films on substrates removed at point F were in the emeraldine oxidation state, consistent with the hypothesis given above. Interestingly, no deposit of polyaniline was observed on substrates immersed in the polymerization bath after the time given in point D.

Qualitatively similar results were obtained using ring and nitrogen substituted derivatives of polyaniline [16], affording thereby, a facile entry into a whole new class of highly oxidized polyanilines.

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REFERENCES

1 A.G. MacDiarmid, J-C. Chiang, A.F. Richter, N.L.D Somasiri and A.J. Epstein, in L. Alcacer (ed.), Conducting Polymers, D. Reidel, Dordrecht, 1987, p. 105.

2 A.F. Richter, A. Ray, K.V. Ramanathan, S.K. Manohar, G.T. Furst, S.J. Opella, A.G. MacDiarmid and A.J. Epstein, Synth. Met., 29 (1989) E243; S. Kaplan, E.M. Conwell, A.F. Richter and A.G. MacDiarmid, ibid., E235.

3 J-C. Chiang,and A.G. MacDiarmid, Synth. Met., 13 (1986) 193.

4 A.G. MacDiarmid and A.J. Epstein, Faraday Trans.and Disc. 88 (1989) 317.

5 P.M. McManus, S.C. Yang and R.J. Cushman, J. Chem. Soc.Chem. Commun. (1985) 1556.

6 G.E. Wnek, Synth. Met., 15 (1986) 213.

7 Y. Sun, A.G. MacDiarmid and A. J. Epstein J. Chem. Soc. Chem. Commun. (1990) 529.

8 S.K. Manohar, A.G. MacDiarmid and A.J. Epstein , Bull Am. Phys. Soc.,34 (1989) 582; S. Miyata and A.Techagumpuch, Synth. Met., 31 (1989) 311.

9 W S. Huang, B.D. Humphrey and A.G. MacDiarmid, J. Chem. Soc. Trans., 82 (1986) 2385.

10 Anal. calcd. for C_6H_4N: C, 79.98; H, 4.48; N; 15.54, Total, 100.00. Found: C, 79.35; H, 4.31; N, 15.41; Total, 99.07%.

11 A.G. Green and A.E. Woodhead, J. Chem. Soc. Trans., 97 (1910) 2388.

12 A.I. Vogel,in Quantitative Inorganic Analysis, Wiley, New York, 1961 p. 298.

13 Anal. calcd. for $C_{24}H_{18}N_4$: C, 79.56; H, 4.97; N, 15.54; Total, 100.00. Found: C, 79.05; H, 4.95; N, 15.30; Total, 99.30.

14 The value of oxidation potential of ammonium persulfate was estimated to be ~1.88V (vs. SCE): F. Minisci; A. Citterio and C. Giordano, Acc. Chem. Res. (1983) 1627. Aqueous 1.0N HCl exhibits an elecrtrochemical window between ~-0.2V and ~1.05V vs. SCE.

15 R.V. Gregory, W.C. Kimbrell and H.H. Kuhn, Synth. Met., 28 (1989) C-823.

16 S.K. Manohar, A.G. MacDiarmid, unpublished observations.