

Stable Aqueous Dispersions of Polyaniline

N. Gospodinova, P. Mokreva and L. Terlemezyan

Institute of Polymers, Bulgarian Academy of Sciences, BG-1113 Sofia, Bulgaria

Relatively concentrated stable aqueous dispersions of polyaniline containing uniform spherical particles have been prepared for the first time using a underivatized poly(vinyl alcohol coacetate) as a steric stabilizer.

Polyaniline (or its derivatives) will probably prove to be among the most useful conducting polymers due to its good thermal and oxidative stability.¹ However, like most conducting polymers prepared to date, it is somewhat intractable and is only slightly soluble in a limited number of solvents, *e.g.* dimethylformamide, dimethyl sulfoxide, *N*-methylpyrrolidone and concentrated sulfuric acid.² An approach to overcoming the processability problem is the preparation of conducting polymers in colloidal form.

Most of the initial more or less unsuccessful attempts to produce colloidal polyaniline (PANI) had to do with physically adsorbed polymeric surfactants. Such is the case of methyl cellulose, poly(vinyl alcohol coacetate) (PVA), poly(vinyl pyrrolidone), poly(vinyl pyridine *co*-*p*-aminostyrene), poly(ethylene oxide) which have resulted in macroscopic precipitation due to inefficient adsorption of the stabilizer, although in certain cases a low yield of colloidal polyaniline has been reported.^{3–5} Recently,⁶ preparation of colloidal fibrils of PANI–poly(acrylic acid) complex by template-guided chemical polymerization has been reported.

To achieve colloidal stability of polyaniline particles another synthetic approach was suggested consisting of graft copolymerization of aniline onto appropriate polymeric surfactants.^{5,7–9} Polyaniline dispersion has been prepared by chemical grafting of polyaniline onto a tailor-made random copolymer poly(2-vinyl pyridine-*co*-*p*-aminostyrene)⁷ or onto PVA, derivatised with pendant aniline groups.⁹ Sterically stabilized polyaniline particles, thus obtained, revealed a non-spherical (rice grain) morphology.

The authors⁵ rationalized that even more efficient steric stabilization could be achieved if a graft copolymer is used, in which the backbone is grafted to the surface, *e.g.* with an acrylate backbone containing pendant polymerisable groups [*e.g.* glycidyl groups and poly(ethylene oxide) chains]. Using this stabilizer at a concentration of 2.8 wt% in solution they found that spherical particles could be prepared, although rather polydisperse in size. To our best knowledge, this is the only paper⁵ concerning the preparation of aqueous dispersions of PANI containing spherical particles. However, the conditions for obtaining the dispersions have not been specified.

The present paper reports preparation of aqueous dispersions of PANI, stabilized by PVA, which have been previously specified in a patent application.¹⁰ It is worth noting that this is the first communication where concentrated stable aqueous dispersions of PANI in the presence of non-modified PVA are described.

The typical synthesis was carried out as follows: into the stirred 100 ml aqueous PVA solution (10 wt%) successively were added 8.4 ml hydrochloric acid (38 wt%), 10 ml aniline and 23 g ammonium persulfate dissolved in 5 ml deionized water (oxidant : aniline molar ratio of 1 : 1). PVA (*M* 72 000, 86 mol% of vinyl alcohol units) was purchased from Fluka. The polymerization was carried out at 0–5 °C for 24 h. The dispersion thus obtained was stable for at least 10 months. Preliminary study of the dispersion using scanning electron microscopy (SEM) revealed relatively uniform spherical particles with an average diameter of 150–200 nm. For the SEM investigation colloidal particles of PANI were separated from the low molecular mass components and the excess of PVA in the reaction mixture by exhaustive dialysis followed by centrifugation.

Using the method described, stable transparent dispersions have been prepared at PVA concentration in aqueous solution 1–10 wt% and aniline concentration in the polymerizing

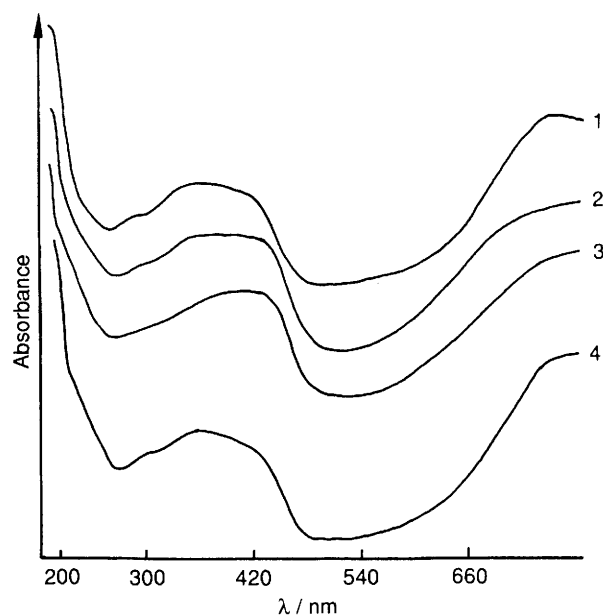


Fig. 1 Optical absorption spectra of dispersions, prepared at various concentrations of aniline in the polymerizing system: 1: 0.25 wt%; 2: 2 wt%; 3: 10 wt% and 4: free standing film cast from dispersion, corresponding to curve 1

system 0.25–10 wt% (aniline : stabilizer ratio 0.025 : 1–1 : 1 by weight) at molar ratio oxidant : aniline of 0.25 : 1–2 : 1.

Dispersions of 1% concentration prepared previously⁹ even in the presence of modified PVA (0.4–1 wt%) were rather unstable and had been separated for several weeks.

Therefore, it could be supposed that the very possibility for preparation as well as the high stability of our dispersions were determined by experimental conditions favourable for grafting of PANI onto PVA, and formation of stable disperse particles. The most important conditions are oxidant used, oxidant : aniline and aniline : stabilizer ratios. The optical absorption spectra of dispersions (Fig. 1), showed the polymerization to proceed with high conversion of aniline.

Comparing absorption spectra of dispersions and of a film cast (Fig. 1), as well of solution and film spectra of emeraldine salt available in ref. 11 it may be stated that the dispersion and the film spectra are closer.

A comparison of optical spectra of PANI dispersion obtained at various concentrations of aniline in the polymerizing system (see Fig. 1) indicates that an increase of aniline concentration in the range 0.25 to 10 wt% (at constant PVA concentration of 10 wt%) results in shifts of absorption maxima towards longer wavelengths. These changes in the spectra could be connected with the corresponding changes both on molecular (molecular mass, oxidation degree) and supermolecular level. All dispersions, however, contained low-molecular-mass (soluble) products. Optical spectrum of such a product is characteristic of aniline oligomers, containing quinoid structure.^{12,13} Deep-green flexible films which contained both the colloidal PANI particles and the excess non-absorbed PVA, were obtained by drying the dispersions. The conductivity of the films was found by the usual four probe method to be 10^{-5} – $1 \Omega^{-1} \text{ cm}^{-1}$ depending on PANI contents (2–50 wt%).

In conclusion it may be stated that we were able to prepare for the first time relatively concentrated stable colloidal dispersions of PANI containing uniform spherical particles (average diameter 150–200 nm) using underivatized poly(vinyl alcohol coacetate) as a steric stabilizer.

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References

- 1 R. B. Kaner, A. G. MacDiarmid, *Sci. Am.*, 1988, **2**, 60.
- 2 S. Li, Y. Cao and Z. Xue, *Synth. Metals*, 1987, **20**, 141.
- 3 J. F. Miller, BSc. Thesis, Univ. of Bristol, UK, 1988 (cited in ref. 8).
- 4 E. C. Cooper, PhD Thesis, Univ. of Bristol, UK, 1987 (cited in ref. 8).
- 5 B. Vincent and J. Waterson, *J. Chem. Soc., Chem. Commun.*, 1990, **9**, 683.
- 6 J.-M. Liu and C. Yang, *J. Chem. Soc., Chem. Commun.*, 1991, **21**, 1529.
- 7 S. P. Armes and M. Aldissi, *J. Chem. Soc., Chem. Commun.*, 1989, **2**, 88.
- 8 S. P. Armes and M. Aldissi, Proceedings of the ACS Division of Polymeric Materials, Science and Engineering, 1989, **60**, 751.
- 9 S. P. Armes, M. Aldissi, S. Agnew and S. Gottesfeld, *Mol. Cryst. Liq. Cryst.*, 1990, **190**, 63.
- 10 N. Gospodinova, P. Mokreva and L. Terlemezyan, *Bulg. Pat. Appl.*, 94859, 1991.
- 11 Y. Cao, P. Smith and A. J. Heeger, *Synth. Metals*, 1989, **32**, 263.
- 12 P. M. McManus, S. Ch. Yang and R. J. Cushman, *J. Chem. Soc., Chem. Commun.*, 1985, 1556.
- 13 Sze-Ming Yang, Woei-Ming Shian and Juh-Jenn Lai, *Synth. Metals*, 1992, **41–43**, 757.