

PREPARATION AND CHARACTERIZATION OF AQUEOUS POLYANILINE DISPERSIONS

NATALIA GOSPODINOVA,¹ LEVON TERLEMEZYAN,¹ PAVLINA MOKREVA,¹ JAROSLAV STEJSKAL²
and PAVEL KRATOCHVIL²

¹Institute of Polymers, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

²Institute of Makromolecular Chemistry, Academy of Sciences of Czech Republic, 162 06 Prague 6,
Czech

(Received 9 December 1992)

Abstract—Stable aqueous dispersions of polyaniline (PANI) have been prepared using an underivatized poly(vinyl alcohol-co-acetate) (PVAL) as a steric stabilizer. Investigation of aqueous PANI dispersions by scanning electron microscopy and light scattering revealed that oxidative polymerization of aniline in the presence of PVAL results in the formation of spherical particles. Their size does not depend on the concentration of aniline in the polymerizing system but the uniformity of the particles seems to be improved as the aniline concentration is increased at least up to a certain limit. Electron absorption spectroscopy study of PANI dispersions made it possible to follow the changes of PANI on both molecular and supermolecular levels. When the initial concentration of aniline in the polymerizing system was *ca* 2 wt% (at a concentration of PVAL from 2 to 10 wt%), electrical conductivity of free standing films cast from dispersions reached 10^{-1} S/cm.

INTRODUCTION

Polyaniline (PANI) (or its derivatives) will probably prove to be among the most useful conducting polymers because of 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 few solvents, e.g. dimethylformamide, dimethyl sulphoxide, *N*-methylpyrrolidone, conc. H_2SO_4 [2]. An approach to overcoming the problem of processability is the preparation of conducting polymers in colloidal form.

Most of the initial attempts to produce colloidal PANI involved polymeric stabilizers, such as methyl cellulose, poly(vinyl alcohol-co-acetate) (PVAL), poly(vinyl pyrrolidone), poly(vinyl pyridine-co-butyl methacrylate), poly(ethylene oxide). They resulted in macroscopic precipitation due to inefficient adsorption of the stabilizer although, in certain cases a low yield of colloidal PANI was reported [3-5]. To achieve colloidal stability of polyaniline particles, another synthetic approach was suggested, consisting of graft copolymerization of aniline (ANI) onto appropriate polymeric stabilizers [5-8]. PANI dispersions have been prepared by chemical grafting of ANI onto polymeric stabilizers containing polymerizable groups in the main chain (such as poly(2-vinyl pyridine-co-p-aminostyrene) [6]), as well as pendant polymerizable groups (such as aniline groups [8], glycidyl groups or poly(ethylene oxide) chains [5]).

We have succeeded in preparing stable aqueous dispersions of PANI with spherical particles < 200 nm, using PVAL as a steric stabilizer [9]. This method enabled us for the first time to follow easily *in situ* by electron absorption spectroscopy (EAS) both the intermediates and the final product [9-11]. EAS is a technique, sensitive to changes in PANI not

only on the molecular but also on the supermolecular level, due to the charge transport mechanism which involves both intramolecular and intermolecular electron transport [12, 13]. For this reason, investigation of PANI dispersions simultaneously by EAS and by a method typically used for characterization of supermolecular structure in solution (light scattering) is of substantial interest. Our previous short communication reported results on the characterization of aqueous dispersions of PANI by light scattering methods [14].

In this paper, results from investigations of aqueous dispersions of PANI at the molecular and supermolecular level by using EAS and light scattering, together with electrical conductivity measurements of free standing films cast from dispersions, are presented and discussed.

EXPERIMENTAL PROCEDURES

Reagent-grade ANI, HCl (38%), ammonium peroxydisulphate, PVAL (molar mass M_w 230,000 g mol⁻¹, 86 mol% of vinyl alcohol units) were purchased from Fluka. ANI was vacuum distilled prior to use.

A typical synthesis was carried out thus: to a stirred 100 ml aqueous PVAL solution (10 wt%), the following components were successively added 8.4 ml of HCl, 2 ml of aniline and 1.15 g of ammonium peroxydisulphate dissolved in 5 ml deionized water (oxidant/ANI molar ratio of 0.25). Polymerization was carried out at 0-5° for 24 hr. Using the method described but modified concentration of ingredients, stable dispersions have been prepared at PVAL concentrations in aqueous solution between 1-10 wt% and aniline concentrations in the polymerizing system in the range 0.25-10 wt% at molar ratios of oxidant/aniline (OX/ANI) from 0.25 to 2.

Electron absorption spectra of dispersions were recorded on a Specord M42 (Carl Zeiss, Germany). The hydrodynamic radii of the dispersion particles were determined with Coulter Nano-Sizer (England), working on the dynamic

light scattering principle. The apparatus allows also estimate of the non-uniformity of the particles.

Prior to preparation of samples for light scattering and scanning electron microscopy (SEM), low-molar mass components of the reaction mixture were removed by exhaustive dialysis. After centrifugation of a dialysed dispersion (2 hr, 20,000 rpm), the sediment was redispersed in water. For SEM investigation, the redispersed particles were diluted with water and a droplet was evaporated on a brass support. Conductivity measurements of free-standing films cast from dispersions were performed using the four-probe technique.

RESULTS AND DISCUSSION

Spherical particles with $R \sim 75-100$ nm were observed by SEM (Fig. 1). Aggregation of some particles occurs during preparation of the sample for SEM; no aggregates were detected in the dispersion by light scattering.

Comparing the absorption spectra of dispersions and of a cast film (Fig. 2), it may be stated that the dispersion and the film spectra are similar. Analysing the experimental data from SEM, light scattering, absorption spectra and noting the absence of macroscopic precipitation in the systems, it could be supposed that PANI is completely contained inside the dispersion particles.

Comparison of absorption spectra of PANI dispersions obtained at fixed concentration of PVAL (10 wt%) and fixed molar ratio OX/ANI (equal to unity) but various concentrations of ANI in the polymerizing system (see Fig. 2), indicates that increase of ANI concentration in the range 0.25–10 wt% results in shifts of absorption maxima towards longer wavelengths. Similar shifts with increasing aniline concentration were observed also at all the other ratios OX/ANI used.

The enhanced absorption in the near i.r. region could be regarded as a result of the changes in PANI

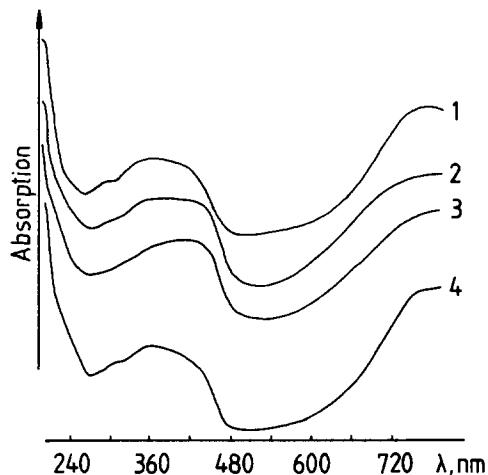


Fig. 2. Absorption spectra of dispersions, prepared at various concentrations of aniline in the polymerizing system: 1, 0.25 wt%; 2, 2 wt%; 3, 10 wt%; 4, free-standing film cast from dispersion, corresponding to curve 1 (concentration of PVAL = 10 wt%, molar ratio OX/ANI = 1).

both on molecular (oxidation level, molecular mass) [10, 12], and supermolecular level (due to decrease of the interchain separation) [15, 16], i.e. as a consequence of the changes in intra- and interchain transport.

It could be expected that the variation of pH of the medium and of the ratio OX/ANI would affect mainly the molecular characteristics of PANI. But the ratio ANI/PVAL (or PANI/PVAL) must affect the conditions of formation of dispersion particles and their characteristics, i.e. the structure of PANI on a supermolecular level.

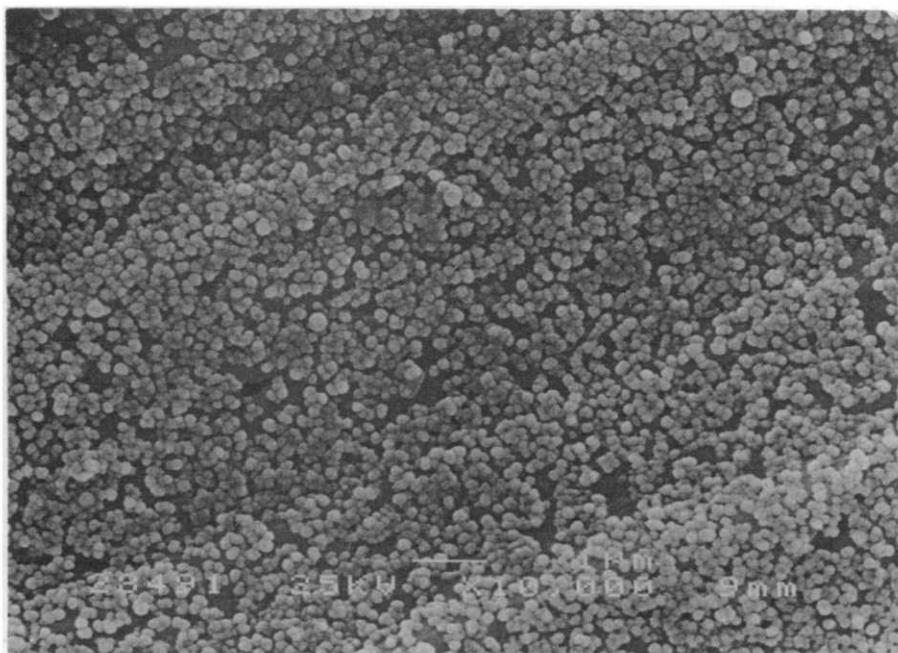


Fig. 1. SEM micrograph of PANI dispersion stabilized by PVAL (concentration of dispersion $c = 1.6 \times 10^{-5}$ g cm $^{-3}$ prior to evaporation, magnification 10,000).

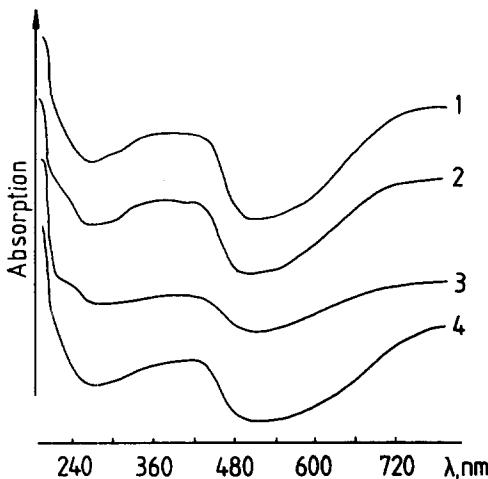


Fig. 3. Absorption spectra of dispersions, prepared at various concentrations of PVAL in the polymerizing system: 1, 10 wt%; 2, 8 wt%; 3, 4 wt%; 4, 2 wt% (concentration of ANI = 2 wt%; molar ratio OX/ANI = 1).

Actually, analogous red shifts of absorption maxima in spectra (including the enhanced absorption in the near i.r.) of dispersions were observed when the aniline concentration (2 wt%) and the molar ratio OX/ANI (equal to unity) were kept constant, while the concentration of PVAL was decreased from 10 to 2 wt% (Fig. 3). Moreover, spectra of dispersions obtained at different ANI concentrations but the same ratio ANI/PVAL were similar (Fig. 2, curve 3 and Fig. 3, curve 4). Hence, it could be suggested that the observed increase of absorption in the near i.r. is a consequence of the changes in PANI at the supermolecular level.

Concerning the colloidal properties, results of dynamic light scattering revealed that the particle size does not practically depend on the concentration of aniline in the reaction system. However, the

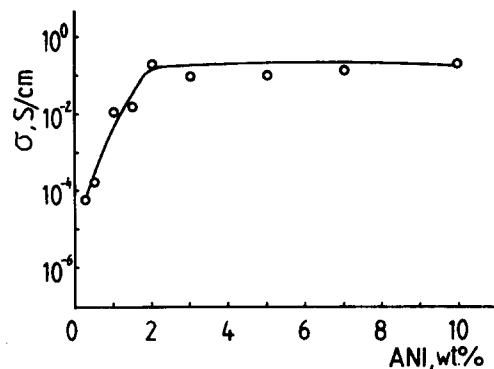


Fig. 4. Electrical conductivity of free standing films cast from dispersions prepared at various ANI concentrations in the polymerizing system.

uniformity of particles seems to improve as the aniline concentration increases, at least up to a certain limit (Table 1). Increasing ratio PANI/PVAL probably leads to the formation of more compact and more uniform particles, where, in the PANI core, intermolecular interactions (and therefore interchain electron transport) is favoured. On the other hand, the formation of a core/shell structure results in better protection of the conductive cores.

A consequence of these changes was the dependence of conductivity of free-standing films cast from dispersions on the ANI/PVAL ratio (Fig. 4). Conductivity sharply increased on raising the ANI content in the polymerizing system up to 1 wt% (concentration of PVAL—10 wt%), i.e. in the range of lower ANI/PVAL ratios, where, as was suggested above, the conditions were not favourable for the formation of particles for which the conductive core was encapsulated in insulating PVAL. During film formation by casting those dispersions, contacts between the cores of these particles became possible, resulting in a sharp increase of conductivity.

Conductivity did not increase as much at higher concentration of ANI in the reaction mixture (2–10 wt%) and did not reach the value for 100%

Table 1. Hydrodynamic radii, R_h , and relative estimates of the non-uniformity, P , for PANI dispersions prepared at various aniline concentrations in the reaction system

Concentration of ANI in the polymerizing system (wt%)	R_h (nm)	P^*
0.25	293	8.0
1.0	173	4.6
1.5	145	4.5
2.0	139	4.3
3.0	131	2.5
5.0	162	1.5
6.0	150	0.3
7.0†	143	0.3
10.0	146	2.4

*On a scale from 0 (uniform particles) to 9 (particles very non-uniform in size).

†A sample shown on a micrograph in Fig. 1. The hydrodynamic radii obtained from light scattering are larger than particle radii from SEM (Fig. 1) because they include the contribution of the PVAL shell.

Polymerization conditions: 10 wt% of PVAL, OX/ANI = 0.5.

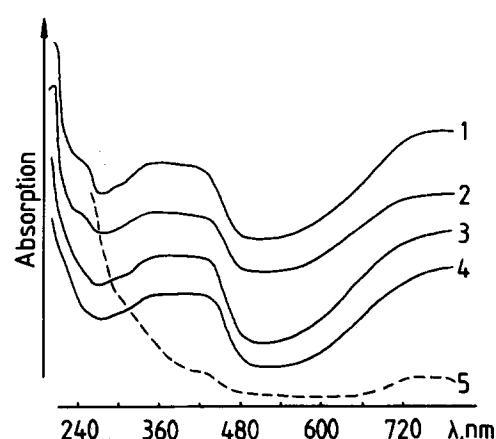


Fig. 5. Absorption spectra of dispersions, prepared at various OX/ANI molar ratios in the polymerizing system: 1, 0.25; 2, 0.4; 3, 1; 4, 1.5; 5, 3 (concentration of PVAL = 10 wt%; concentration of aniline = 2 wt%).

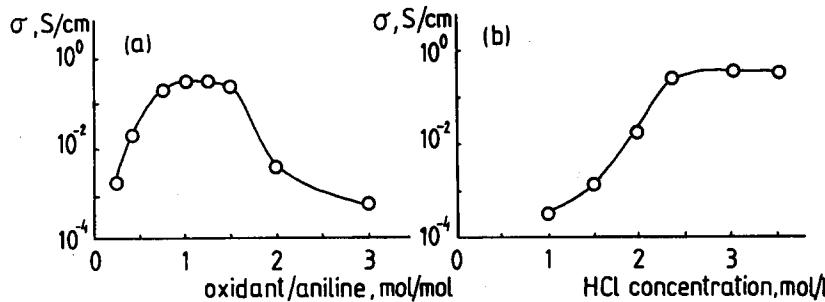


Fig. 6. Electrical conductivity of free standing films cast from dispersions, prepared at various OX/ANI molar ratios (a) and concentrations of HCl (b) in the polymerizing system.

PANI ($\sigma = 10\text{--}12 \text{ S/cm}$), prepared under similar conditions in the absence of PVAL. Probably, this effect resulted from the prevention of physical contact of conductive PANI cores by means of the non-conductive PVAL shells because of the formation of core/shell structure of the dispersion particles.

Qualitative changes in the absorption spectra were not observed during wide variation of the ratio OX/ANI (0.25–1) (Fig. 5). Considerable changes in the shape of the spectrum were found only at OX/ANI ratio of three. Slight long-wave shifts of the absorption maxima at higher OX/ANI ratios showed that oxidant concentration, at least in the range studied, has very slight effect on the spectra of PANI dispersion.

The variation of conductivity of the films cast from dispersions obtained at different OX/ANI ratios [Fig. 6(a)], is related probably to the conversion of aniline (yield of PANI), as well as to the oxidation level of PANI. Comparatively lower conductivities of films cast from dispersions prepared at low oxidant concentration [Fig. 6(a)] are due probably to lower aniline conversion (Fig. 5, curves 1 and 2). Absorption at 254 nm is characteristic of aniline hydrochloride and decreased from curve 1 to curve 4.

The oxidation level of PANI could be estimated by the ratio of absorbances at 777 and 580 nm (A_{777}/A_{580}) [17].

As seen from Table 2, considerable overoxidation of PANI proceeded at OX/ANI ratios > 1.5 . This effect resulted in qualitative changes in the absorption spectrum of PANI and in decreased conductivity of films cast from dispersions.

Variation of HCl concentration from 1 to 4 M did not result in any qualitative changes in the absorption spectrum of PANI (Fig. 7). Decreased conductivity of films cast from dispersion prepared at HCl

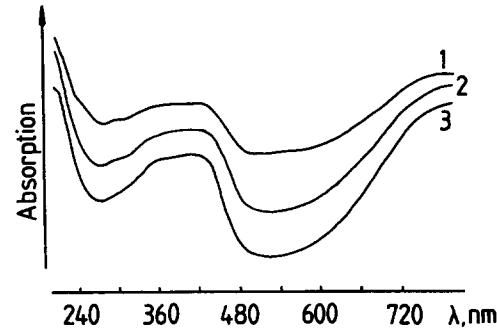


Fig. 7. Absorption spectra of dispersions, prepared at various concentrations of HCl: 1, 1 M; 2, 1.5 M; 3, 2 M, 2.3 M, 4 M (concentration of PVAL = 10 wt%; OX/ANI molar ratio = 1).

concentration < 2.3 M [Fig. 6(b)] was perhaps a result of lower aniline conversion.

CONCLUSIONS

Investigation of aqueous PANI dispersions by using SEM and light scattering revealed that oxidative polymerization of ANI in the presence of PVAL as a steric stabilizer results in the formation of spherical particles. Their size does not depend on the concentration of aniline in the polymerizing system but the uniformity of particles seems to be improved as the ANI concentration is increased, at least up to a certain limit. EAS study of PANI dispersions made it possible to follow the changes of PANI on both molecular and supermolecular levels. When the initial concentration of aniline in the polymerizing system was *ca* 2 wt% (at concentrations of PVAL from 2 to 10 wt%), electrical conductivity of free standing films cast from dispersions reached 10^{-1} S/cm .

Table 2. Dependence of oxidation level of PANI (determined by the ratio of absorbances at 777 and 580 nm) on the ratio OX/ANI

Oxidant/aniline, molar ratio	A_{777}/A_{580}
0.25	2.70
0.40	2.30
0.75	2.30
1.00	2.40
1.50	2.70
3.00	1.33

REFERENCES

1. R. B. Kaner and A. G. MacDiarmid. *Sci. Am.* **2**, 60 (1988).
2. S. Li, Y. Cao and Z. Xue. *Synth. Met.* **20**, 141 (1987).
3. J. F. Miller. B. Sc. Thesis, University of Bristol, U.K. (1988) (cited in Ref. 8).
4. E. C. Cooper. Ph.D. Thesis, University of Bristol, U.K. (1987) (cited in Ref. 8).
5. B. Vincent and J. Waterson. *J. Chem. Soc., Chem. Commun.* **9**, 683 (1990).

6. S. P. Armes and M. Aldissi. *J. Chem. Soc., Chem. Commun.* **2**, 88 (1989).
7. S. P. Armes and M. Aldissi. *Proceedings of the ACS Division of Polymeric Materials, Science and Engineering*, **60**, 751 (1989).
8. S. P. Armes, M. Aldissi, S. Agnev and S. Gottesfeld. *Molec. Cryst. Liq. Cryst.* **190**, 63 (1990).
9. N. Gospodinova, P. Mokreva and L. Terlemezyan. *J. Chem. Soc., Chem. Commun.* **13**, 923 (1992).
10. N. Gospodinova, P. Mokreva and L. Terlemezyan. *Polym. Commun.* (in press).
11. N. Gospodinova, L. Terlemezyan, P. Mokreva and K. Kossev. *Polym. Commun.* (in press).
12. Y. Cao, P. Smith and A. J. Heeger. *Synth. Metals* **32**, 263 (1989).
13. W. Fock, C. Wnek and Y. Wei. *J. Phys. Chem.* **91**, 5813 (1987).
14. J. Stejskal, P. Kratochvil, N. Gospodinova, L. Terlemezyan and P. Mokreva. *Polym. Commun.* **33**, 4857 (1993).
15. A. P. Monkman and P. Adams. *Synth. Met.* **41-43**, 891 (1991).
16. Y. Cao, G. M. Treacy, P. Smith and A. J. Heeger. *Appl. Phys. Lett.* **60**, 2711 (1992).
17. M. Morita and J. Hashida. *J. appl. Polym. Sci.* **41**, 1073 (1990).